Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement VIII, Halogen Species[a]
IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry

R. Atkinson[b]

Air Pollution Research Center, Department of Environmental Sciences, and Department of Chemistry, University of California, Riverside, California 92521

D. L. Baulch

School of Chemistry, University of Leeds, Leeds LS2 9JT, England

R. A. Cox

Department of Chemistry, Centre for Atmospheric Science, University of Cambridge, Cambridge CB2 1EW, England

R. F. Hampson, Jr.

Chemical Kinetics Data Center, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

J. A. Kerr(Chairman)

School of Chemistry, University of Birmingham, Birmingham B15 2TT, England

M. J. Rossi

Laboratoire de Pollution Atmosphérique et Sol (LPAS, IGR), Ecole Polytechnique Federale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

J. Troe

Institute of Physical Chemistry, University of Göttingen, D-37077 Göttingen, Germany

This paper updates and extends part of the previous data base of critical evaluations of the kinetics and photochemistry of gas-phase chemical reactions of neutral species involved in atmospheric chemistry [J. Phys. Chem. Ref. Data **9**, 295 (1980); **11**, 327 (1982); **13**, 1259 (1984); **18**, 881 (1989); **21**, 1125 (1992); **26**, 521 (1997); **26**, 1329 (1997); **28**, 191 (1999)]. The present evaluation is limited to the inorganic halogen family of atmospherically important reactions. The work has been carried out by the authors under the auspices of the IUPAC Subcommittee on Gas Phase Kinetic Data Evaluation for Atmospheric Chemistry. Data sheets have been prepared for 102 thermal and photochemical reactions, containing summaries of the available experimental data with notes giving details of the experimental procedures. For each thermal reaction, a preferred value of the rate coefficient at 298 K is given together with a temperature dependence where possible. The selection of the preferred value is discussed and estimates of the accuracies of the rate coefficients and temperature coefficients have been made for each reaction. For each photochemical reaction the data sheets list the preferred values of the photoabsorption cross sections and the quantum yields of the photochemical reactions together with comments on how they were selected. The data sheets are intended to provide the basic physical chemical data needed as input for calculations that model

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atmospheric chemistry. A table summarizing the preferred rate data is provided, together with an appendix listing the available values of enthalpies of formation of the reactant and product species. © *2000 American Institute of Physics.* [S0047-2689(00)00302-0]

Contents

1. Preface

This paper is Supplement VIII to the original set of critically evaluated kinetic and photochemical rate parameters for atmospheric chemistry, published by the CODATA Task Group on Gas Phase Chemical Kinetics in 1980[1] and subsequently updated by Supplement I in 1982[2] and Supplement II in 1984.[3] The original evaluation and Supplements I and II were primarily intended to furnish a kinetic data base for modeling middle atmosphere chemistry (10–55 km altitude).

In 1985 the International Union of Pure and Applied Chemistry (IUPAC) set up a group to continue and enlarge upon the work initiated by CODATA. The Subcommittee on Gas Phase Kinetic Data Evaluation for Atmospheric Chemistry is chaired by J. A. Kerr and is part of the Commission on Chemical Kinetics (I.4) of the IUPAC Physical Chemistry Division.

This subcommittee produced Supplement III in 1989,[4] Supplement IV in 1992,[5] Supplements V and VI in 1997,[6,7] and Supplement VII in 1999,[8] in which the original data base was extended and updated to include more reactions involved in tropospheric chemistry. Since it was not possible to cope with all of the very large number of chemical reac-

tions involved in tropospheric chemistry, it was originally decided to limit the coverage to those organic reactions for which kinetic or photochemical data exist for species containing up to three carbon atoms.

With the publication of Supplement V in 1997,[6] the data base had become so extensive that the Subcommittee decided that future supplements would be limited to dealing in turn with parts of the set of over 700 gas-phase and heterogeneous reactions. To this end Supplement VI was an update and extension of the O_x, HO_x, NO_x, and SO_x gas-phase reactions, and Supplement VII was an update and extension of the reactions of organic species (including the C_4 organic reactions resulting from the atmospheric oxidation of *n*-butane). Supplement VIII continues this policy by updating and extending a selection of the most important reactions of atmospheric inorganic halogen species, last reviewed in Supplement V; the reactions of organic halogen-containing organics have been extensively reviewed by the most recent NASA evaluation,[9] and the reactions of FO_x, ClO_x, BrO_x and IO_x species with organic compounds were reviewed in Supplement VII. In the case of photochemical reactions of halogen species, here we limit our considerations to iodine species, in view of the extensive treatment of the photochemical reactions of chlorine and bromine species in the most recent NASA evaluation.[9]

Following the pattern of Supplements V,[6] VI,[7] and VII,[8] here we provide a data sheet for each of the reactions of the families considered. Each data sheet provides a preferred rate coefficient, together with a statement of the assigned uncertainty limits, a comment giving the basis for the recommendation, and a list of the relevant references. Supplement VIII also lists the data used in the selection of the Preferred Values for each reaction. This means that in Supplement VIII some of the earlier data, omitted during the development of Supplements I–V, have been re-entered on the data sheets. This change, initiated with Supplement VI, is intended to aid the reader in appreciating how the Preferred Values were selected. To the extent that this information suffices, the reader can use the present publication without need to refer to the previous publications in the series. However, it should be emphasized that in preparing the updated data sheets, we have not listed all of the previous data contained in the original evaluation[1] and Supplements I–V.[2–6] Consequently, for many reactions, to obtain the complete data set and historical background to the preferred rate parameters, it is recommended that the present supplement be read in conjunction with its predecessors.[1–6]

The cutoff point for literature searching for this supplement was June, 1999. As in our previous evaluations, we also include data which were available to us in preprint form at that point.

2. Gas Phase Reactions—Summary of Reactions and Preferred Rate Data

Gas-Phase Reactions—Summary of Reactions and Preferred Rate Data

Page No.	Reaction	k_{298} (cm³ molecule⁻¹ s⁻¹)	$\Delta \log k_{298}$[a]	Temp. dependence of (k/cm³ molecule⁻¹ s⁻¹)	Temp. (range/K)	$\Delta(E/R)/K$[a]
	FOx Reactions					
178	$O+FO\rightarrow O_2+F$	2.7×10^{-11}	±0.3			
178	$O+FO_2\rightarrow O_2+FO$	5×10^{-11}	±0.7			
178	$F+H_2\rightarrow HF+H$	2.4×10^{-11}	±0.1	$1.1\times10^{-10}\exp(-450/T)$	190–380	±100
179	$F+H_2O\rightarrow HF+HO$	1.4×10^{-11}	±0.1	1.4×10^{-11}	240–380	±200
180	$F+O_2+M\rightarrow FO_2+M$ (k_0)	$5.8\times10^{-33}[N_2]$	±0.3	$5.8\times10^{-33}(T/300)^{-1.7}[N_2]$	100–380	$\Delta n=\pm0.5$
	(k_∞)	1.2×10^{-10}	±0.3	1.2×10^{-10}	100–380	$\Delta \log k=\pm0.3$
		$F_c=0.5$		$F_c=0.5$	100–380	
182	$FO_2+M\rightarrow F+O_2+M$ (k_0/s^{-1})	$1.5\times10^{-17}[N_2]$	±0.3	$8.4\times10^{-9}(T/300)^{-1.25}\exp(-5990/T)[N_2]$	310–420	±500; $\Delta n=\pm0.5$
	(k_∞/s^{-1})	3.1×10^5	±0.3	$1.7\times10^{14}(T/300)^{0.45}\exp(-5990/T)$	310–420	±500; $\Delta n=\pm0.5$
		$F_c=0.5$		$F_c=0.5$	310–420	
183	$F+O_3\rightarrow FO+O_2$	1.0×10^{-11}	±0.25	$2.2\times10^{-11}\exp(-230/T)$	250–370	±200
184	$F+HONO_2\rightarrow HF+NO_3$	2.3×10^{-11}	±0.1	$6.0\times10^{-12}\exp(400/T)$	260–320	±200
184	$FO+O_3\rightarrow$ products	$<1\times10^{-14}$				
185	$FO+NO\rightarrow F+NO_2$	2.2×10^{-11}	±0.15	$8.2\times10^{-12}\exp(300/T)$	290–850	±200
186	$FO+FO\rightarrow$ products	1.0×10^{-11}	±0.2	1.0×10^{-11}	290–440	±250
186	$FO_2+O_3\rightarrow$ products	$<4\times10^{-16}$				
187	$FO_2+NO\rightarrow FNO+O_2$	7.5×10^{-13}	±0.3	$7.5\times10^{-12}\exp(-690/T)$	190–300	±400
187	$FO_2+NO_2\rightarrow$ products	4.0×10^{-14}	±0.3	$3.8\times10^{-11}\exp(-2040/T)$	260–320	±500
188	$FO_2+CO\rightarrow$ products	$<6\times10^{-16}$				
	ClOx Reactions					
188	$O+HOCl\rightarrow HO+ClO$	1.7×10^{-13}	±0.5	1.7×10^{-13}	210–300	±300
189	$O+ClO\rightarrow Cl+O_2$	3.8×10^{-11}	±0.1	3.8×10^{-11}	210–430	±250
190	$O+OClO\rightarrow O_2+ClO$	1.0×10^{-13}	±0.3	$2.4\times10^{-12}\exp(-960/T)$	240–400	±300
191	$O+OClO+M\rightarrow ClO_3+M$ (k_0)	$1.8\times10^{-31}[N_2]$	±0.3	$1.8\times10^{-31}(T/298)^{-1}[N_2]$	240–320	$\Delta n=\pm0.5$
	(k_∞)	3.1×10^{-11}	±0.3	$3.1\times10^{-11}(T/298)^1$	240–320	$\Delta n=\pm1$
		$F_c=0.48$				
192	$O+Cl_2O\rightarrow ClO+ClO$	4.5×10^{-12}	±0.15	$2.7\times10^{-11}\exp(-530/T)$	230–380	±200
193	$O+ClONO_2\rightarrow$ products	2.2×10^{-13}	±0.08	$4.5\times10^{-12}\exp(-900/T)$	200–330	±150
194	$Cl+H_2\rightarrow HCl+H$	1.7×10^{-14}	±0.1	$3.9\times10^{-11}\exp(-2310/T)$	200–310	±200
195	$Cl+HO_2\rightarrow HCl+O_2$	3.2×10^{-11}	±0.2	$1.8\times10^{-11}\exp(170/T)$	250–420	±250
	$\rightarrow ClO+HO$	9.1×10^{-12}	±0.3	$4.1\times10^{-11}\exp(-450/T)$	250–420	±250
196	$Cl+H_2O_2\rightarrow HCl+HO_2$	4.1×10^{-13}	±0.2	$1.1\times10^{-11}\exp(-980/T)$	260–430	±500
197	$Cl+O_2+M\rightarrow ClOO+M$ (k_0)	$1.4\times10^{-33}[N_2]$	±0.2	$1.4\times10^{-33}(T/300)^{-2.9}[N_2]$	160–300	$\Delta n=\pm1$
	(k_0)	$1.6\times10^{-33}[O_2]$	±0.2	$1.6\times10^{-33}(T/300)^{-2.9}[O_2]$	160–300	$\Delta n=\pm1$
198	$ClOO+M\rightarrow Cl+O_2+M$ (k_0/s^{-1})	$6.2\times10^{-13}[N_2]$	±0.3	$2.8\times10^{-10}\exp(-1820/T)[N_2]$	160–300	±200
198	$Cl+CO+M\rightarrow ClCO+M$ (k_0)	$1.3\times10^{-33}[N_2]$	±0.3	$1.3\times10^{-33}(T/300)^{-3.8}[N_2]$	180–300	$\Delta n=\pm0.5$
199	$ClCO+M\rightarrow Cl+CO+M$ (k_0/s^{-1})	$2.0\times10^{-14}[N_2]$	±0.4	$4.1\times10^{-10}\exp(-2960/T)[N_2]$	180–300	±200

Gas-Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page No.	Reaction	k_{298} (cm³ molecule⁻¹ s⁻¹)	$\Delta \log k_{298}$ [a]	Temp. dependence of $(k/\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1})$	Temp. (range/K)	$\Delta(E/R)/K$ [a]
200	Cl+O₃→ClO+O₂	1.2×10^{-11}	±0.06	$2.9 \times 10^{-11}\exp(-260/T)$	200–300	±100
201	Cl+HONO₂→HCl+NO₃	$<2.0 \times 10^{-16}$				
202	Cl+NO₃→ClO+NO₂	2.4×10^{-11}	±0.2	2.4×10^{-11}	200–300	±400
202	Cl+OClO→ClO+ClO	5.7×10^{-11}	±0.1	$3.2 \times 10^{-11}\exp(170/T)$	220–430	±200
203	Cl+Cl₂O→Cl₂+ClO	9.6×10^{-11}	±0.1	$6.2 \times 10^{-11}\exp(130/T)$	230–380	±130
204	Cl+Cl₂O₂→Cl₂+ClOO	1.0×10^{-10}	±0.3	1.0×10^{-10}	230–300	±300
204	Cl+ClONO₂→Cl₂+NO₃	1.0×10^{-11}	±0.10	$6.5 \times 10^{-12}\exp(135/T)$	190–360	±50
205	HO+Cl₂→HOCl+Cl	6.5×10^{-14}	±0.08	$3.6 \times 10^{-12}\exp(-1200/T)$	230–360	±300
206	HO+HCl→H₂O+Cl	8.0×10^{-13}	±0.06	$1.8 \times 10^{-12}\exp(-240/T)$	200–300	±100
207	HO+HOCl→ClO+H₂O	5.0×10^{-13}	±0.5			
208	HO+ClO→HO₂+Cl / →HCl+O₂	1.9×10^{-11}	±0.2	$7.7 \times 10^{-12}\exp(270/T)$	200–380	±150
209	HO+OClO→HOCl+O₂	6.6×10^{-12}	±0.3	$4.5 \times 10^{-13}\exp(800/T)$	290–480	±200
210	HO+ClNO₂→HOCl+NO₂	3.6×10^{-14}	±0.3	$2.4 \times 10^{-12}\exp(-1250/T)$	260–350	±300
210	HO+ClONO₂→products	4.0×10^{-13}	±0.2	$1.2 \times 10^{-12}\exp(-330/T)$	240–390	±200
211/212	NO₃+HCl→HNO₃+Cl	$<5 \times 10^{-17}$				
212	ClO+HO₂→HOCl+O₂ / →HCl+O₃	5.0×10^{-12}	±0.15	$4.6 \times 10^{-13}\exp(710/T)$	230–300	±300
213	ClO+O₃→ClOO+O₂ / →OClO+O₂	$<1.5 \times 10^{-17}$ / $<1 \times 10^{-18}$				
213	ClO+NO→Cl+NO₂	1.7×10^{-11}	±0.1	$6.2 \times 10^{-12}\exp(295/T)$	200–420	±100
214	ClO+NO₂+M→ClONO₂+M (k_0) (k_∞) $F_c=0.5$	$1.6 \times 10^{-31}[\text{N}_2]$ / 1.5×10^{-11}	±0.1 / ±0.3	$1.6 \times 10^{-31}(T/300)^{-3.4}[\text{N}_2]$ / 1.5×10^{-11} / $F_c=\exp(-T/430)$	250–350 / 250–350 / 250–350	$\Delta n=\pm 1$ / $\Delta \log k=\pm 0.3$
215	ClO+NO₃→ClOO+NO₂ / →OClO+NO₂	4.6×10^{-13}	±0.2	4.6×10^{-13}	210–360	±400
216	ClO+ClO→Cl₂+O₂ / →Cl+ClOO / →Cl+OClO	4.8×10^{-15} / 8.0×10^{-15} / 3.5×10^{-15}	±0.2 / ±0.2 / ±0.2	$1.0 \times 10^{-12}\exp(-1590/T)$ / $3.0 \times 10^{-11}\exp(-2450/T)$ / $3.5 \times 10^{-13}\exp(-1370/T)$	260–390 / 260–390 / 260–390	±500 / ±500 / ±500
218	ClO+ClO+M→Cl₂O₂+M (k_0) (k_∞) $F_c=0.6$	$1.7 \times 10^{-32}[\text{N}_2]$ / 5.4×10^{-12}	±0.1 / ±0.3	$1.7 \times 10^{-32}(T/300)^{-4}[\text{N}_2]$ / 5.4×10^{-12} / $F_c=0.6$	190–390 / 190–390 / 190–390	$\Delta n=\pm 1.5$ / $\Delta \log k=\pm 0.3$
219	Cl₂O₂+M→ClO+ClO+M (k_0/s^{-1}) (k_∞/s^{-1}) $F_c=0.6$	$2.2 \times 10^{-18}[\text{N}_2]$ / 6.7×10^2	±0.3 / ±0.3	$1 \times 10^{-6}\exp(-8000/T)[\text{N}_2]$ / $4.8 \times 10^{15}\exp(-8820/T)$ / $F_c=0.6$	260–310 / 260–310 / 260–310	±900 / ±500
220	ClO+OClO+M→Cl₂O₃+M (k_0) (k_∞) $F_c=0.6$	$6.2 \times 10^{-32}[\text{N}_2]$ / 2.4×10^{-11}	±0.3 / ±0.3	$6.2 \times 10^{-32}(T/300)^{-4.7}[\text{N}_2]$ / 2.4×10^{-11} / $F_c=0.6$	200–300 / 200–300 / 200–300	$\Delta n=\pm 1$ / $\Delta \log k=\pm 0.3$
222	Cl₂O₃+M→ClO+OClO+M (k_0/s^{-1}; 226 K)	$2.8 \times 10^{-18}[\text{N}_2]$	±0.5 (226 K)			
222	OClO+O₃→ClO₃+O₂	3.0×10^{-19}	±0.4	$2.1 \times 10^{-12}\exp(-4700/T)$	260–300	±1000
223	OClO+NO→ClO+NO₂	3.4×10^{-13}	±0.3			
223	OClO+NO₃+M→O₂ClONO₂+M (k_0; 220 K)	$1 \times 10^{-31}[\text{He}]$				
224	Cl₂O₂+O₃→ClO+ClOO+O₂	$<1 \times 10^{-19}$ (200 K)				

Gas-Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page No.	Reaction	k_{298} (cm³ molecule⁻¹ s⁻¹)		$\Delta \log k_{298}$[a]	Temp. dependence of $(k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	Temp. (range)/K	$\Delta(E/R)/K$[a]
	BrO_x Reactions						
224	O+HOBr→HO+BrO	2.8×10^{-11}		±0.2	$1.2\times10^{-10}\exp(-430/T)$	230–430	±300
225	O+BrO→O₂+Br	4.1×10^{-11}		±0.2	$1.9\times10^{-11}\exp(230/T)$	230–330	±150
225	Br+HO₂→HBr+O₂	2.0×10^{-12}		±0.3	$1.4\times10^{-11}\exp(-590/T)$	260–390	±200
226	Br+H₂O₂→HBr+HO₂ } →HOBr+HO	$<5\times10^{-16}$					
226	Br+O₃→BrO+O₂	1.2×10^{-12}		±0.08	$1.7\times10^{-11}\exp(-800/T)$	190–430	±200
227	Br+NO₂+M→products+M	$4.2\times10^{-31}[N_2]$	(k_0)	±0.3	$4.2\times10^{-31}(T/300)^{-2.4}[N_2]$	250–350	$\Delta n=\pm1$
		2.7×10^{-11}	(k_∞)	±0.4	2.7×10^{-11}	250–350	$\Delta \log k=\pm0.4$
		$F_c=0.55$					
228	Br+OClO→BrO+ClO	3.5×10^{-13}		±0.3	$2.7\times10^{-11}\exp(-1300/T)$	260–430	±300
229	Br+Cl₂O→BrCl+ClO	4.3×10^{-12}		±0.1	$2.1\times10^{-11}\exp(-470/T)$	220–410	±200
229	Br+Cl₂O₂→BrCl+ClOO	3.0×10^{-12}		±0.3			
230	HO+HBr→H₂O+Br	1.1×10^{-11}		±0.10	1.1×10^{-11}	200–420	$\Delta \log k=\pm0.1$
231	HO+Br₂→HOBr+Br	4.3×10^{-11}		±0.10	$1.9\times10^{-11}\exp(240/T)$	230–360	±150
231	HO+BrO→products	7.5×10^{-11}		±0.5			
232	Br+NO₃→BrO+NO₂	1.6×10^{-11}		±0.3			
232	BrO+NO₃→BrOO+NO₂	1.0×10^{-12}		±0.5			
233	NO₃+HBr→HNO₃+Br	$<1\times10^{-16}$					
234	BrO+HO₂→HOBr+O₂ } →HBr+O₃	2.3×10^{-11}		±0.4	$3.7\times10^{-12}\exp(545/T)$	210–350	±100
235	BrO+O₃→products	$<2\times10^{-17}$					
236	BrO+NO→Br+NO₂	2.1×10^{-11}		±0.1	$8.7\times10^{-12}\exp(260/T)$	220–430	±100
236	BrO+NO₂+M→BrONO₂+M	$4.7\times10^{-31}[N_2]$	(k_0)	±0.1	$4.7\times10^{-31}(T/300)^{-3.1}[N_2]$	240–350	$\Delta n=\pm1$
		1.4×10^{-11}	(k_∞)	±0.1	$1.4\times10^{-11}(T/300)^{-1.2}$	240–350	$\Delta n=\pm1$
		$F_c=0.40$			$F_c=\exp(-T/327)$	240–350	
238	BrO+ClO→Br+OClO	6.8×10^{-12}		±0.1	$1.6\times10^{-12}\exp(430/T)$	220–400	±200
	→Br+ClOO	6.1×10^{-12}		±0.1	$2.9\times10^{-12}\exp(220/T)$	220–400	±200
	→BrCl+O₂	1.0×10^{-12}		±0.1	$5.8\times10^{-13}\exp(170/T)$	220–400	±200
240	BrO+BrO→2Br+O₂	2.7×10^{-12}		±0.1	2.7×10^{-12}	250–390	±200
	→Br₂+O₂	4.8×10^{-13}		±0.1	$2.9\times10^{-14}\exp(840/T)$	250–390	±200
	IO_x Reactions						
242	O+I₂→IO+I	1.4×10^{-10}		±0.15			
242	O+IO→O₂+I	1.4×10^{-10}		±0.2			
243	I+HO₂→HI+O₂	3.8×10^{-13}		±0.3	$1.5\times10^{-11}\exp(-1090/T)$	280–360	±500
244	I+O₃→IO+O₂	1.2×10^{-12}		±0.15	$1.9\times10^{-11}\exp(-830/T)$	230–370	±150
244	I+NO+M→INO+M	$1.8\times10^{-32}[N_2]$	(k_0)	±0.1	$1.8\times10^{-32}(T/300)^{-1.0}[N_2]$	290–450	$\Delta n=\pm0.5$
		1.7×10^{-11}	(k_∞)	±0.5	1.7×10^{-11}	300–400	$\Delta \log k=\pm0.5$
		$F_c=0.6$					
246	I+NO₂+M→INO₂+M	$3.0\times10^{-31}[N_2]$	(k_0)	±0.2	$3.0\times10^{-31}(T/300)^{-1}[N_2]$	290–450	$\Delta n=\pm1$
		6.6×10^{-11}	(k_∞)	±0.3	6.6×10^{-11}	290–450	$\Delta \log k=\pm0.3$
		$F_c=0.63$					
247	I+NO₃→IO+NO₂	No recommendation (see data sheet)					
247	I₂+NO₃→I+IONO₂	1.5×10^{-12}		±0.3	1.5×10^{-12}	290–430	$\Delta \log k=\pm0.3$

Gas-Phase Reactions—Summary of Reactions and Preferred Rate Data—Continued

Page No.	Reaction	k_{298} (cm³ molecule⁻¹ s⁻¹)	$\Delta \log k_{298}$ [a]	Temp. dependence of $(k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	Temp. (range/K)	$\Delta(E/R)/K$ [a]
248	HO+HI→H₂O+I	7.0×10^{-11}	±0.3	1.6×10^{-11} exp(440/T)	240–360	±400
249	HO+I₂→HOI+I	2.1×10^{-10}	±0.15	2.1×10^{-10}	240–350	±300
249	NO₃+HI→HNO₃+I	No recommendation (see data sheet)				
250	IO+HO₂→HOI+O₂	8.8×10^{-11}	±0.2	9.0×10^{-12} exp(680/T)	270–380	±300
251	IO+ClO→products	1.2×10^{-11}	±0.1	4.7×10^{-12} exp(280/T)	200–370	±100
252	IO+BrO→products	8.5×10^{-11}	±0.1	1.5×10^{-11} exp(510/T)	200–390	±350
254	IO+IO→products	9.1×10^{-11}	±0.1	5.0×10^{-11} exp(180/T)	250–320	±100
255	IO+NO→I+NO₂	2.1×10^{-11}	±0.2	9.0×10^{-12} exp(260/T)	240–370	±150
256	IO+NO₂+M→IONO₂+M	$7.7 \times 10^{-31}[\text{N}_2]$ (k_0)	±0.3	$7.7 \times 10^{-31}(T/300)^{-5}[\text{N}_2]$	250–360	$\Delta n = \pm 2$
		1.6×10^{-11} (k_∞)	±0.3	1.6×10^{-11}	250–360	$\Delta \log k = \pm 0.3$
		$F_c = 0.4$		$F_c = 0.4$	250–360	
257	INO+INO→I₂+2NO	1.3×10^{-14}	±0.4	8.4×10^{-11} exp(−2620/T)	300–450	±600
258	INO₂+INO₂→I₂+2NO₂	4.7×10^{-15}	±0.5	2.9×10^{-11} exp(−2600/T)	290–350	±1000
258	HOI+hν→products	See data sheet				
259	IO+hν→products	See data sheet				
261	INO+hν→products	See data sheet				
261	INO₂+hν→products	See data sheet				
262	IONO₂+hν→products	See data sheet				

[a]The cited uncertainty is an expanded uncertainty corresponding appoximately to a 95% confidence limit.

3. Guide to the Data Sheets

3.1. Gas-Phase Reactions

The data sheets are principally of two types: (i) those for individual thermal reactions and (ii) those for the individual photochemical reactions.

3.1.1. Thermal Reactions

The data sheets begin with a statement of the reactions including all pathways that are considered feasible. This is followed by the corresponding enthalpy changes at 298 K, calculated from the enthalpies of formation summarized in the Appendix.

The available kinetic data on the reactions are summarized under two headings: (i) Absolute Rate Coefficients, and (ii) Relative Rate Coefficients. Under these headings, we include new data that have been published since the last complete IUPAC evaluation[6] as well as the data used in deriving the preferred values. Under both of the headings above, the data are presented as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature-dependent form over a stated temperature range. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form, $k = A \exp(-B/T)$, where $B = E/R$. For a few bimolecular reactions, we have listed temperature dependences in the alternative form, $k = A' T^{-n}$ or $CT^n \exp(-D/T)$, where the original authors have found this to give a better fit to their data. For pressure-dependent combination and dissociation reactions, the non-Arrhenius temperature dependence is used. This is discussed more fully in a subsequent section of the Introduction.

Single temperature data are presented as such and wherever possible the rate coefficient at, or close to, 298 K is quoted directly as measured by the original authors. This means that the listed rate coefficient at 298 K may differ slightly from that calculated from the Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked with an asterisk indicate that the value was calculated by extrapolation of a measured temperature range which did not include 298 K. The tables of data are supplemented by a series of comments summarizing the experimental details. The following list of abbreviations, relating to experimental techniques, is used in the Techniques and Comments sections:

A   — absorption
AS   — absorption spectroscopy
CCD   — coupled charge detector
CIMS   — chemical ionization mass spectroscopy/
          spectrometric
CL   — chemiluminescence
DF   — discharge flow
EPR   — electron paramagnetic resonance
F   — flow system
FP   — flash photolysis
FTIR   — Fourier transform infrared

FTS   — Fourier transform spectroscopy
GC   — gas chromatography/gas chromatographic
HPLC   — high-performance liquid chromatography
IR   — infrared
LIF   — laser induced fluorescence
LMR   — laser magnetic resonance
LP   — laser photolysis
MM   — molecular modulation
MS   — mass spectrometry/mass spectrometric
P   — steady state photolysis
PLP   — pulsed laser photolysis
PR   — pulse radiolysis
RA   — resonance absorption
RF   — resonance fluorescence
RR   — relative rate
S   — static system
TDLS   — tunable diode laser spectroscopy
UV   — ultraviolet
UVA   — ultraviolet absorption
VUVA   — vacuum ultraviolet absorption

For measurements of relative rate coefficients, wherever possible the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different from that reported by the original author owing to a different choice of rate coefficient of the reference reaction. Whenever possible the reference rate data are those preferred in the present evaluation.

The preferred rate coefficients are presented (i) at a temperature of 298 K and (ii) in temperature-dependent form over a stated temperature range.

This is followed by a statement of the uncertainty limits in $\log k$ at 298 K and the uncertainty limits either in (E/R) or in n, for the mean temperature in the range. Some comments on the assignment of uncertainties are given later in this introduction.

The "Comments on Preferred Values" describe how the selection was made and give any other relevant information. The extent of the comments depends upon the present state of our knowledge of the particular reaction in question. The data sheets are concluded with a list of the relevant references.

3.1.2. Conventions Concerning Rate Coefficients

All of the reactions in the table are elementary processes. Thus the rate expression is derived from a statement of the reaction, e.g.,

$$A + A \rightarrow B + C$$
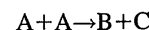
$$-\frac{\frac{1}{2}d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]^2$$

Note that the stoichiometric coefficient for A, i.e., 2, appears in the denominator before the rate of change of [A] (which is equal to $2k[A]^2$) and as a power on the right-hand side.

Representations of k as a function of temperature characterize simple "direct" bimolecular reactions. Sometimes it is found that k also depends on the pressure and the nature of the bath gas. This may be an indication of complex formation during the course of the bimolecular reaction, which is always the case in combination reactions. In the following sections the representations of k, which are adopted in these cases, are explained.

3.1.3. Treatment of Combination and Dissociation Reactions

Unlike simple bimolecular reactions such as those considered in Sec. 3.1.2, combination reactions

$$A+B+M \rightarrow AB+M$$
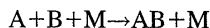
and the reverse dissociation reactions

$$AB+M \rightarrow A+B+M$$
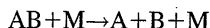
are composed of sequences of different types of physical and chemical elementary processes. Their rate coefficients reflect the more complicated sequential mechanism and depend on the temperature T and the nature and concentration of the third body $[M]$. In this evaluation, the combination reactions are described by a formal second-order rate law

$$\frac{d[AB]}{dt} = k[A][B]$$

while dissociation reactions are described by a formal first-order rate law

$$\frac{-d[AB]}{dt} = k[AB]$$

In both cases, k depends on the temperature and on $[M]$.

In order to rationalize the representations of the rate coefficients used in this evaluation, we first consider the Lindemann–Hinshelwood reaction scheme. The combination reactions follow an elementary mechanism of the form

$$A+B \rightarrow AB^* \qquad (1)$$

$$AB^* \rightarrow A+B \qquad (-1)$$

$$AB^* + M \rightarrow AB+M \qquad (2)$$

while the dissociation reactions are characterized by

$$AB+M \rightarrow AB^* +M \qquad (-2)$$

$$AB^* +M \rightarrow AB+M \qquad (2)$$

$$AB^* \rightarrow A+B \qquad (-1)$$

Assuming quasistationary concentrations for the highly excited unstable species AB^* (i.e., that $d[AB^*]/dt \sim 0$), it follows that the rate coefficient for the combination reaction is given by

$$k=k_1\left(\frac{k_2[M]}{k_{-1}+k_2[M]}\right)$$

while that for the dissociation reaction is given by

$$k=k_{-2}[M]\left(\frac{k_{-1}}{k_{-1}+k_2[M]}\right)$$

In these equations the expressions before the parentheses represent the rate coefficients of the process initiating the reaction, whereas the expressions within the parentheses denote the fraction of reaction events which, after initiation, complete the reaction to products.

In the low-pressure limit ($[M] \rightarrow 0$) the rate coefficients are proportional to $[M]$; in the high pressure limit ($[M] \rightarrow \infty$) they are independent of $[M]$. It is useful to express k in terms of the limiting low pressure and high pressure rate coefficients

$$k_0 = \frac{\lim k([M])}{[M] \rightarrow 0}$$

and

$$k_\infty = \frac{\lim k([M])}{[M] \rightarrow \infty}$$

respectively. From this convention, the Lindemann–Hinshelwood equation is obtained

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty}$$

It follows that for combination reactions, $k_0 = k_1 k_2[M]/k_{-1}$ and $k_\infty = k_1$, while for dissociation reactions, $k_0 = k_{-2}[M]$ and $k_\infty = k_{-1}k_{-2}/k_2$. Since detailed balancing applies, the ratio of the rate coefficients for combination and dissociation at a fixed T and $[M]$ is given by the equilibrium constant $K_c = k_1 k_2/k_{-1}k_{-2}$.

Starting from the high pressure limit, the rate coefficients fall off with decreasing third body concentration $[M]$, and the corresponding representation of k as a function of $[M]$ is termed the "falloff curve" of the reaction. In practise, the above Lindemann–Hinshelwood expressions do not suffice to characterize the falloff curves completely. Because of the multistep character of the collisional deactivation ($k_2[M]$) and activation ($k_{-2}[M]$) processes, and energy- and angular momentum dependences of the association (k_1) and dissociation (k_{-1}) steps, as well as other phenomena, the falloff expressions have to be modified. This can be done by including a broadening factor F to the Lindemann–Hinshelwood expression[10-12]

$$k=\left(\frac{k_0 k_\infty}{k_0+k_\infty}\right)F = k_0\left(\frac{1}{1+k_0/k_\infty}\right)F = k_\infty\left(\frac{k_0/k_\infty}{1+k_0/k_\infty}\right)F$$

The broadening factor F depends on the ratio k_0/k_∞, which is proportional to $[M]$, and can be used as a measure of "reduced pressure." At not too high a temperature, F is approximately given by[10-12]

$$\log F \cong \frac{\log F_c}{1+[\log(k_0/k_\infty)]^2}$$

With increasing temperature, a better representation is obtained[10-12] by replacing $[\log(k_0/k_\infty)]^2$ by $[\log(k_0/k_\infty)/N]^2$ with $N=\{0.75-1.27\log F_c\}$. The "center broadening fac-

tor'' F_c generally decreases with increasing molecular complexity of AB and with increasing temperature. The value of F_c can be calculated from unimolecular rate theory;[10-12] alternatively it is often obtained by fitting experimental falloff curves. To a crude approximation, the temperature dependence of F_c is represented by

$$F_c \cong \exp(-T/T^*),$$

which is used in this evaluation. An even simpler policy was chosen in Ref. 9 where a temperature independent standard value of $F_c = 0.6$ was adopted. This choice, however, often oversimplifies the representation.

The rate coefficients for combination or dissociation in this evaluation are characterized by the three parameters k_0, k_∞, and F_c (and the equations given above). If an experimental falloff curve is fitted to these three quantities, changes in F_c will also change the limiting k_0- and k_∞-values. Therefore, a falloff representation requires the specification of all three of the parameters k_0, k_∞, and F_c, which is applied throughout this evaluation. It should also be noted that unimolecular rate theory allows for at least semiquantitative predictions of F_c, k_0, and k_∞ (see, for example, Ref. 10). For combination reactions the dependence of k_0 and k_∞ on the temperature T is represented in this evaluation in the form

$$k \propto T^{-n}$$

except for cases with an established energy barrier in the potential. We have chosen this form of temperature dependence because it usually gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. Obviously, the relevant values of n are different for k_0 and k_∞. In this evaluation, values of k_0 are given for selected examples of third bodies M, and if possible for M=N_2, O_2 or air.

3.1.4. Treatment of Complex-Forming Bimolecular Reactions

Bimolecular reactions may follow the ''direct'' pathway

$$A+B \rightarrow C+D$$
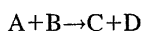
and/or involve complex formation.

$$A+B \rightleftarrows AB^* \rightarrow C+D$$
$$\downarrow M$$
$$AB$$
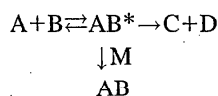
We designate the rate coefficients of the individual steps as in Sec. 3.1.3. above

$$A+B \rightarrow AB^* \qquad (1)$$

$$AB^* \rightarrow A+B \qquad (-1)$$

$$AB^* + M \rightarrow AB + M \qquad (2)$$

$$AB^* \rightarrow C+D \qquad (3)$$
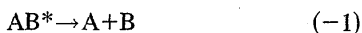
Assuming quasistationary concentrations of AB^* (i.e., $d[AB^*]/dt \sim 0$), a Lindemann–Hinshelwood type of analysis leads to

$$\frac{d[AB]}{dt} = k_S[A][B]$$

$$\frac{d[C]}{dt} = k_D[A][B]$$

$$\frac{d[A]}{dt} = (k_S + k_D)[A][B]$$

where

$$k_S = k_1 \left(\frac{k_2}{k_{-1} + k_2 + k_3} \right)$$

$$k_D = k_1 \left(\frac{k_3}{k_{-1} + k_2 + k_3} \right)$$

Note that since k_2 is proportional to [M], k_S and k_D are dependent on the nature and concentration of the third body M, in addition to their temperature dependence. In reality, as for the combination and dissociation reactions, the given expressions for k_S and k_D have to be extended by suitable broadening factors F in order to account for the multistep character of process (2) and the energy dependences of processes (1), (−1) and (3). These broadening factors, however, differ from those for combination and dissociation reactions. For simplicity, they are ignored in this evaluation such that k_D at high pressure approaches

$$k_D \Rightarrow k_1 k_3 / k_2$$

which is inversely proportional to [M]. k_D may also be expressed by

$$k_D \approx k_{D0} k_S / k_{S0}$$

where k_{D0} and k_{S0} are the respective limiting low pressure rate coefficients for the formation of C+D or A+B at the considered [M]. When it is established that complex formation is involved, this equation is used to characterize the increasing suppression of C+D formation with increasing [M].

3.1.5. Photochemical Reactions

The data sheets begin with a list of feasible primary photochemical transitions for wavelengths usually down to 170 nm, along with the corresponding enthalpy changes at 0 K where possible or alternatively at 298 K, calculated from the data in the Appendix. Calculated threshold wavelengths corresponding to these enthalpy changes are also listed, bearing in mind that the values calculated from the enthalpy changes at 298 K are not true ''threshold values.''

This is followed by tables summarizing the available experimental data concerning: (i) absorption cross sections and (ii) quantum yields. These data are supplemented by a series of comments.

The next table lists the preferred absorption cross-section data and the preferred quantum yields at appropriate wavelength intervals. For absorption cross sections the intervals are usually 1, 5, or 10 nm. Any temperature dependence of

the absorption cross sections is also given where possible. The aim in presenting these preferred data is to provide a basis for calculating atmospheric photolysis rates. For absorption continua the temperature dependence is often represented by Sulzer–Wieland type expressions.[13]

The comments again describe how the preferred data were selected and include other relevant points. The photochemical data sheets are also concluded with a list of references.

3.1.6. Conventions Concerning Absorption Cross Sections

These are presented in the data sheets as "absorption cross sections per molecule, base e." They are defined according to the equations

$$I/I_0 = \exp(-\sigma[N]l),$$

$$\sigma = \{1/([N]l)\}\ln(I_0/I),$$

where I_0 and I are the incident and transmitted light intensities, σ is the absorption cross section per molecule (expressed in this paper in units of cm^2), [N] is the number concentration of absorber (expressed in molecule cm^{-3}), and l is the path length (expressed in cm). Other definitions and units are frequently quoted. The closely related quantities "absorption coefficient" and "extinction coefficient" are often used, but care must be taken to avoid confusion in their definition; it is always necessary to know the units of concentration and of path length and the type of logarithm (base e or base 10) corresponding to the definition. To convert an absorption cross section to the equivalent Naperian (base e) absorption coefficient (expressed in cm^{-1}) of a gas at a pressure of 1 standard atm and temperature of 273 K, multiply the value of σ in cm^2 by 2.69×10^{19}.

3.1.7. Assignment of Uncertainties

Under the heading "reliability," estimates have been made of the absolute accuracies of the preferred values of k at 298 K and of the preferred values of E/R over the quoted temperature range. The accuracy of the preferred rate coefficient at 298 K is quoted as the term $\Delta \log k$, where $\Delta \log k = D$ and D is defined by the equation, $\log_{10} k = C \pm D$. This is equivalent to the statement that k is uncertain to a factor of F, where $D = \log_{10} F$. The accuracy of the preferred value of E/R is quoted as the term $(\Delta E/R)$, where $(\Delta E/R) = G$ and G is defined by the equation $E/R = H \pm G$. D and G are expanded uncertainties corresponding approximately to a 95% confidence limit.

For second-order rate coefficients listed in this evaluation, an estimate of the uncertainty at any given temperature within the recommended temperature range may be obtained from the equation:

$$\Delta \log k(T) = \Delta \log k(298\,\text{K}) + 0.4343\left|\frac{\Delta E}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right|.$$

The assignment of these absolute uncertainties in k and E/R is a subjective assessment of the evaluators. They are not determined by a rigorous, statistical anlysis of the data

base, which is generally too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experimental measurements, the potential for systematic errors, and the number of studies conducted and their agreement or lack thereof. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, i.e., the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 90% confidence limits of $\pm 10\%$ or less are frequently reported in the literature. Unfortunately, when evaluators come to compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients often differ by a factor of 2 or even more. This can only mean that one or more of the studies has involved large systematic uncertainties which are difficult to detect. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

The arbitrary assignment of uncertainties made here is based mainly on our state of knowledge of a particular reaction which is dependent upon factors such as the number of independent investigations carried out and the number of different techniques used. On the whole, our assessment of uncertainty limits tends toward the cautious side. Thus, in the case where a rate coefficient has been measured by a single investigation using one particular technique and is unconfirmed by independent work, we suggest that minimum uncertainty limits of a factor of 2 are appropriate.

In contrast to the usual situation for the rate coefficients of thermal reactions, where intercomparison of results of a number of independent studies permits a realistic assessment of reliability, for many photochemical processes there is a scarcity of apparently reliable data. Thus, we do not feel justified at present in assigning uncertainty limits to the parameters reported for the photochemical reactions.

3.2. Acknowledgments

the preparation of this evaluation. Special thanks go to Christy J. LaClaire for her outstanding efforts in the preparation of this manuscript, before her sudden death in April 1999.

3.3. References to Introduction

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[2] D. L. Baulch, R. A. Cox, P. J. Crutzen, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement I, CODATA Task Group on Chemical Kinetics, J. Phys. Chem. Ref. Data 11, 327 (1982).

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4. Gas-Phase Reactions—Data Sheets

4.1. Fluorine Species

O+FO→O$_2$+F
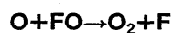
$\Delta H^\circ = -279 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.2) \times 10^{-11}$	298	Bedzhanyan et al., 1993[1]	DF-LMR (a)

Comments

(a) Pseudo-first-order decays of FO radicals in the presence of excess O(^{3}P) atoms were monitored by LMR. O(^{3}P) atom concentrations were determined by EPR.

Preferred Values

$k = 2.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the results of the study of Bedzhanyan et al.,[1] the sole study of this reaction. The temperature dependence of the rate constant is expected to be small for such an atom–radical process, as for the analogous ClO radical reaction.

References

[1] Yu. R. Bedzhanyan, E. M. Markin, G. G. Politenkova, and Yu. M. Gershenzon, Kinet. Catal. **33**, 797 (1993); original pages 998–1003 (1992).

O+FO$_2$→O$_2$+FO
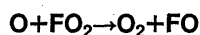
$\Delta H^\circ = -166 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data: no available experimental data.

Preferred Values

$k = 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.7$ at 298 K.

Comments on Preferred Values

There are no experimental data for this reaction. The rate constant for such a radical–atom process is expected to approach the gas collision frequency and is not expected to exhibit a strong temperature dependence.

F+H$_2$→HF+H
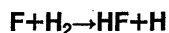
$\Delta H^\circ = -134.7 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.0 \times 10^{-10} \exp[-(433 \pm 50)/T]$	190–373	Wurzberg and Houston, 1980[1]	PLP-CL
$(2.27 \pm 0.18) \times 10^{-11}$	298		
$(2.55 \pm 0.11) \times 10^{-11}$	298	Clyne and Hodgson, 1985[2]	DF-LIF
$1.2 \times 10^{-10} \exp[-(470 \pm 30)/T]$	221–376	Stevens, Brune, and Anderson, 1989[3]	DF-RF (a)
$(2.48 \pm 0.09) \times 10^{-11}$	298		

Comments

(a)   Discharge flow system. F atoms were converted to D atoms by reaction with D_2 downstream of the reaction zone, and the D atoms monitored by resonance fluorescence.

Preferred Values

$k = 2.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.1 \times 10^{-10}$ exp($-450/T$) cm^3 molecule^{-1} s^{-1} over the temperature range 190–380 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

This evaluation accepts the recommended values given in the critical review of Persky and Kornweitz[4] of the literature data for this reaction. The preferred values are based on the results of Wurzberg and Houston,[1] Clyne and Hodgson,[2] and Stevens *et al.*[3]

References

[1] E. Wurzberg and P. L. Houston, J. Chem. Phys. **72**, 4811 (1980).
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[3] P. S. Stevens, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **93**, 4068 (1989).
[4] A. Persky and H. Kornweitz, Int. J. Chem. Kinet. **29**, 67 (1997).

$F + H_2O \rightarrow HF + HO$

$\Delta H° = -71.6$ kJ·mol^{-1}

Rate coefficient data

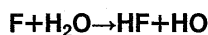| k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
4.2×10^{-11}exp[$-(400 \pm 70)/T$]	243–369	Walther and Wagner, 1983[1]	DF-MS
$(1.1 \pm 0.1) \times 10^{-11}$	300		
$(1.3 \pm 0.1) \times 10^{-11}$	298	Frost *et al.*, 1986[2]	PLP-CL (a)
1.6×10^{-11}exp[$-(28 \pm 42)/T$]	240–373	Stevens, Brune, and Anderson, 1989[3]	DF-RF (b)
$(1.42 \pm 0.06) \times 10^{-11}$	298		

Comments

(a)   Pulsed laser photolysis at 308 nm; HF chemiluminescence monitored.
(b)   Discharge flow system. F atoms were converted to D atoms by reaction with D_2 downstream of the reaction zone. D atoms were monitored by resonance fluorescence.

Preferred Value

$k = 1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 240–380 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The recommended temperature-independent value is based on the results reported by Stevens *et al.*[3] This value is in good agreement with the room temperature results of Walther and Wagner[1] and Frost *et al.*[2] Walther and Wagner,[1] in a limited temperature study, reported an E/R value of 400 K. Although their data[1] have not been used in the derivation of the preferred values, with the exception of the one low temperature (243 K) data point they are within the stated uncertainties.

References

[1] C. D. Walther and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **87**, 403 (1983).
[2] R. J. Frost, D. S. Green, M. K. Osborn, and I. W. M. Smith, Int. J. Chem. Kinet. **18**, 885 (1986).
[3] P. S. Stevens, W. H. Brune, and J. G. Anderson, J. Phys. Chem. **93**, 4068 (1989).

$$F+O_2+M \rightarrow FO_2+M$$

$\Delta H^\circ = -53.3 \text{ kJ} \cdot \text{mol}^{-1}$

Low-pressure rate coefficients

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.2 \times 10^{-34} \exp(656/T)$ [He]	272–362	Zetzsch, 1973[1]	DF-MS (a)
4.7×10^{-33} [He]	298		
$(7 \pm 2) \times 10^{-33}$ [He]	293	Arutyunov, Popov, and Chaikin, 1976[2]	DF-EPR (b)
$(1.4 \pm 0.4) \times 10^{-32}$ [N$_2$]	293		
$(6 \pm 2) \times 10^{-33}$ [Ar]	293		
$(5.4 \pm 0.6) \times 10^{-33}$ [He]	298	Chen *et al.*, 1977[3]	FP (c)
$(1.5 \pm 0.3) \times 10^{-32}$ [O$_2$]	298		
$(5.0 \pm 0.6) \times 10^{-33}$ [F$_2$]	298		
$(8.4 \pm 0.9) \times 10^{-33}$ [Ar]	298		
$2.8 \times 10^{-34} \exp(906/T)$ [Ar]	223–293	Shamonima and Kotov, 1979[4]	DF-EPR (d)
$(6.1 \pm 1.8) \times 10^{-33}$ [Ar]	293		
$(1.0 \pm 0.3) \times 10^{-32}$ [O$_2$]	298	Chebotarev, 1979[5]	PLP (e)
$(4.3 \pm 0.4) \times 10^{-33} (T/300)^{-1.6}$ [Ar]	295–359	Pagsberg *et al.*, 1987[6]	PR (f)
$(2.8 \pm 0.2) \times 10^{-33}$ [He]	298	Lyman and Holland, 1988[7]	PLP (g)
$(3.1 \pm 0.2) \times 10^{-33}$ [Ar]	298		
1.4×10^{-32} [SF$_6$]	295	Ellermann *et al.*, 1994[8]	PR (h)
$5.8 \times 10^{-33} (T/300)^{-1.7}$ [N$_2$]	100–373	Campuzano-Jost *et al.*, 1995[9]	PLP (i)

Comments

(a) Detection of F atoms and FO$_2$ radicals.

(b) Detection of F atoms.

(c) Detection of vibrationally excited HF by IR chemiluminescence.

(d) Detection of F atoms in the presence of excess O$_2$ and Ar. Experimental conditions were varied over only limited ranges; for example, [O$_2$] was varied by a factor of 2 and the total pressure was fixed. The third-order rate coefficient reported for Ar as the diluent gas may be somewhat overestimated as the O$_2$ ranged from ~12% to ~25% of the total pressure. The stoichiometry was assumed to be 2 (i.e., $-d[\text{F}]/dt = 2k[\text{F}][\text{O}_2][\text{M}]$) due to secondary removal of atomic fluorine by reaction with the primary product FO$_2$.

(e) Photolysis of WF$_6$–H$_2$–O$_2$–He mixtures at ~200 nm, with detection of HF by IR chemiluminescence. The relative efficiencies of M were reported to be O$_2$:Ar = 1.4:1.0.

(f) Experiments were carried out in Ar–F$_2$–O$_2$ mixtures with detection of FO$_2$ by absorption at 220 nm. The rate coefficient and the equilibrium constant were determined by varying the O$_2$ concentration. A value of $\Delta H^\circ(298 \text{ K}) = -52.8 \text{ kJ mol}^{-1}$ was derived.

(g) Photolysis of F$_2$ at 248 nm in the presence of O$_2$ and bath gases. The reaction mechanism with six reactions was followed via the analysis of transient absorption signals at 215 nm. The forward and backward rate coefficients of the reactions F+O$_2$+M→FO$_2$+M and

F+FO$_2$+M→F$_2$O$_2$+M were determined. A value of $\Delta H^\circ(298 \text{ K}) = -(56.4 \pm 1.7) \text{ kJ mol}^{-1}$ was derived.

(h) Experiments with SF$_6$–O$_2$ mixtures at 0.20–1.0 bar total pressure with kinetic UV spectroscopic detection of FO$_2$ radicals between 215 and 254 nm. Falloff extrapolations were made with $F_c = 0.6$.

(i) FO$_2$ radicals were detected by UV absorption. Experiments were carried out at total pressures up to 1000 bar of the bath gases He, Ar, and N$_2$. Measurements of the equilibrium constant lead to $\Delta H^\circ(0 \text{ K}) = -49.8 \text{ kJ mol}^{-1}$. Falloff extrapolations were made with F_c near 0.5.

Preferred Values

$k_0 = 5.8 \times 10^{-33} (T/300)^{-1.7}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 100–380 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

Because of the large data base from the study of Campuzano-Jost *et al.*,[9] their rate coefficients values are preferred and are in reasonable agreement with earlier work. Falloff curves were constructed with F_c near 0.5.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.0×10^{-12}	295	Ellermann et al., 1994[8]	PR (a)
1.2×10^{-10}	100–373	Campuzano-Jost et al., 1995[9]	PLP (b)

Comments

(a) See comment (h) for k_0.

(b) See comment (i) for k_0.

Preferred Values

$k_\infty = 1.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 100–380 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 100–380 K.

Comments on Preferred Values

Because of the large pressure range studied by Campuzano-Jost et al.,[9] a reliable falloff extrapolation toward k_∞ was possible. The data of Campuzano-Jost et al.[9] are therefore preferred together with values of F_c near 0.5.

Intermediate Falloff Range

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	P/Torr	M	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients					
2.4×10^{-13}	600 mbar	SF$_6$	298	Wallington and Nielsen, 1991[10]	PR (a)
$(2.35 \pm 0.2) \times 10^{-13}$	600 mbar	SF$_6$	298	Wallington et al., 1992[11]	PR (b)

Comments

(a) Experiments were carried out in mixtures of SF$_6$ and O$_2$ (6.1–20 mbar). FO$_2$ radicals were monitored by UV absorption at 220 nm.

(b) Experiments were carried out in mixtures of SF$_6$ and O$_2$ (2.5–15 mbar). FO$_2$ radicals were monitored by UV absorption at 220 nm. The results were analyzed together with those of Lyman and Holland.[7]

References

[1] C. Zetzsch, *First European Symposium on Combustion*, edited by F. S. Weinberg (Academic London, 1973), p. 35.

[2] V. S. Arutyunov, L. S. Popov, and A. M. Chaikin, Kinet. Catal. **17**, 251 (1976).

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[6] P. Pagsberg, E. Ratajczak, A. Sillesen, and J. T. Jodkowski, Chem. Phys. Lett. **141**, 88 (1987).

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[8] T. Ellermann, J. Sehested, O. J. Nielsen, P. Pagsberg, and T. J. Wallington, Chem. Phys. Lett. **218**, 287 (1994).

[9] P. Campuzano-Jost, A. E. Croce, H. Hippler, M. Siefke, and J. Troe, J. Chem. Phys. **102**, 5317 (1995).

[10] T. J. Wallington and O. J. Nielsen, Int. J. Chem. Kinet. **23**, 785 (1991).

[11] T. J. Wallington, M. M. Maricq, T. Ellermann, and O. J. Nielsen, J. Phys. Chem. **96**, 982 (1992).

$FO_2+M \rightarrow F+O_2+M$

$\Delta H^\circ = 53.3 \text{ kJ} \cdot \text{mol}^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.8 \times 10^{-17}[\text{Ar}]$	295	Pagsberg *et al.*, 1987[1]	PR (a)
$3.1 \times 10^{-17}[\text{Ar}]$	312.5		
$2.8 \times 10^{-16}[\text{Ar}]$	359		
$(2.5 \pm 1.0) \times 10^{-18}[\text{He}]$	298	Lyman and Holland, 1988[2]	PLP (b)
$1.0 \times 10^{-5}T^{-1.25}\exp(-5990/T)[\text{N}_2]$	315–420	Campuzano-Jost *et al.*, 1995[3]	PLP (c)
$1.5 \times 10^{-17}[\text{N}_2]$	298		

Comments

(a) Experiments were carried out in $\text{Ar}-\text{F}_2-\text{O}_2$ mixtures with detection of FO_2 by absorption at 220 nm. The rate of approach to equilibrium was monitored and the equilibrium constant measured. A value of ΔH° (298 K) = 52.8 kJ mol^{-1} was derived by a third-law analysis.

(b) Photolysis of F_2 at 248 nm in the presence of O_2 and bath gases. Transient absorptions at 215 nm were monitored and the approach to equilibrium was analyzed. A value of ΔH° (298 K) = 56.4 kJ mol^{-1} was derived.

(c) The kinetics were followed by monitoring the FO_2 radical by UV absorption. Experiments were carried out between 100 and 375 K at total pressures between 1 and 1000 bar, and in the bath gases He, Ar, and N_2. Measurements of the equilibrium constant lead to ΔH° (0 K) = 49.8 kJ mol^{-1}. Falloff extrapolations were carried out with a value of F_c near 0.5. The expression for k_0 was derived from the recombination rate coefficients of the reverse reaction and the equilibrium constants.

Preferred Values

$k_0 = 1.5 \times 10^{-17} [\text{N}_2] \text{ s}^{-1}$ at 298 K.

$k_0 = 8.4 \times 10^{-9} (T/300)^{-1.25}\exp(-5990/T) [\text{N}_2] \text{ s}^{-1}$ over the temperature range 310–420 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$.

$\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The results of Campuzano-Jost *et al.*[3] are in reasonable agreement with those of Pagsberg *et al.*,[1] but differ at 298 K by a factor of 6 with the data from Lyman and Holland.[2] The preferred values are based on the data of Campuzano-Jost *et al.*[3]

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.3 \times 10^{13}T^{0.45}\exp(-5990/T)$	315–420	Campuzano-Jost *et al.*, 1995[3]	PLP (a)

Comments

(a) See comment (c) for k_0.

Preferred Values

$k_\infty = 3.1 \times 10^5 \text{ s}^{-1}$ at 298 K.

$k_\infty = 1.7 \times 10^{14} (T/300)^{0.45}\exp(-5990/T) \text{ s}^{-1}$ over the temperature range 310–420 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

Because of the large pressure range studied by Campuzano-Jost *et al.*,[3] a reliable falloff extrapolation to-

ward k_∞ was possible. The data of Campuzano-Jost *et al.*[3] are therefore preferred, together with F_c values near 0.5.

References

[1] P. Pagsberg, E. Ratajczak, A. Sillesen, and J. T. Jodkowski, Chem. Phys. Lett. **141**, 88 (1987).

[2] J. L. Lyman and R. Holland, J. Phys. Chem. **92**, 7232 (1988).

[3] P. Campuzano-Jost, A. E. Croce, H. Hippler, M. Siefke, and J. Troe, J. Chem. Phys. **102**, 5317 (1995).

$F+O_3 \rightarrow FO+O_2$
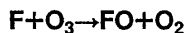
$\Delta H° = -113$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.8 \times 10^{-11} \exp[-(226 \pm 200)/T]$	253–365	Wagner, Zetzsch, and Warnatz, 1972[1]	DF-MS (a)
1.3×10^{-11}	298		
$(6.2 \pm 0.3) \times 10^{-12}$	298	Bedzhanyan, Markin, and Gershenzon, 1993[2]	DF-LMR (b)

Comments

(a) MS detection of O_3 decay in the presence of an excess of F atoms. The temporal profiles of F, FO, and O_3 were monitored by MS.

(b) Discharge flow system with excess of O_3 over F atoms. Rate of formation of FO radicals was monitored by LMR.

Preferred Values

$k = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.2 \times 10^{-11} \exp(-230/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–370 K.

Reliability

$\Delta \log k = \pm 0.25$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred room temperature value is the average of the 298 K values from the two studies of Wagner *et al.*[1] and Bedzhanyan *et al.*[2] The temperature dependence is taken from Wagner *et al.*[1] and the A factor is fitted to the preferred 298 K value. The preferred value at room temperature is supported by values of k derived indirectly in studies of the reactions of CF$_3$O and CF$_3$O$_2$ radicals with O$_3$ by Nielsen and Sehested[3] and Maricq and Szente.[4]

References

[1] H. Gg. Wagner, C. Zetzsch, and J. Warnatz, Ber. Bunsenges. Phys. Chem. **76**, 526 (1972).

[2] Yu. R. Bedzhanyan, E. M. Markin, and Yu. M. Gershenzon, Kinet. Catal. **33**, 594 (1993); original pages 744–752 (1992).

[3] O. J. Nielsen and J. Sehested, Chem. Phys. Lett. **213**, 433 (1993).

[4] M. M. Maricq and J. J. Szente, Chem. Phys. Lett. **213**, 449 (1993).

$F+HONO_2 \rightarrow HF+NO_3$
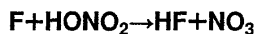
$\Delta H^\circ = -143.9 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.7\pm0.5)\times10^{-11}$	298	Mellouki, Le Bras, and Poulet, 1987[1]	DF-EPR
$(2.1\pm1)\times10^{-11}$	298	Rahman *et al.*, 1988[2]	DF-MS
$6.0\times10^{-12}\exp[(400\pm120)/T]$	260–320	Wine, Wells, and Nicovich, 1988[3]	PLP-A (a)
$(2.3\pm0.1)\times10^{-11}$	298		
$(2.2\pm0.2)\times10^{-11}$	298	Becker *et al.*, 1991[4]	DF-MS/EPR

Comments

(a) Pulsed laser photolysis at 351 nm, with detection of NO_3 radicals by long-path laser absorption at 662 nm. At higher temperatures (335–373 K) the rate coefficient was found to be independent of temperature with a value of $(2.0\pm0.3)\times10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1}$.

### Preferred Values

$k = 2.3\times10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1}$ at 298 K.

$k = 6.0\times10^{-12}\exp(400/T)\text{ cm}^3\text{ molecule}^{-1}\text{s}^{-1}$ over the temperature range 260–320 K.

Reliability

$\Delta \log k = \pm0.1$ at 298 K.
$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

The recommendation is based on the results of the temperature-dependent study of Wine *et al.*,[3] and the room temperature results of Mellouki *et al.*,[1] Rahman *et al.*,[2] and Becker *et al.*[4] The values at room temperature are in good agreement. The study of Wine *et al.*[3] was over the temperature range 260–373 K; below 320 K the authors fitted their data with the Arrhenius expression recommended here, whereas at higher temperatures a temperature-independent value was found, suggesting the occurrence of different mechanisms in the two temperature regimes.

References

[1] A. Mellouki, G. Le Bras, and G. Poulet, J. Phys. Chem. **91**, 5760 (1987).

[2] M. M. Rahman, E. Becker, Th. Benter, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **92**, 91 (1988).

[3] P. H. Wine, J. R. Wells, and J. M. Nicovich, J. Phys. Chem. **92**, 2223 (1988).

[4] E. Becker, Th. Benter, R. Kampf, R. N. Schindler, and U. Wille, Ber. Bunsenges. Phys. Chem. **95**, 1168 (1991).

$FO+O_3 \rightarrow F+2O_2$ (1)

$\rightarrow FO_2+O_2$ (2)
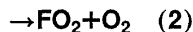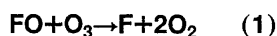
$\Delta H^\circ(1) = -172 \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta H^\circ(2) = -226 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<1.2\times10^{-12}$	298	Sehested *et al.*, 1994[1]	PR-UVA (a)
$<1\times10^{-14}$	298	Li, Friedl, and Sander, 1995[2]	DF-MS (b)

Comments

(a) Pulse radiolysis-UV absorption spectroscopy technique at 18 bar total pressure. FO_2 radicals and O_3 were monitored in absorption at 220 and 288 nm, respectively.

(b) Discharge flow-mass spectrometric technique at 1 mbar total pressure. FO radicals were produced in the reaction of F atoms with excess O_3. No appreciable decay of FO radicals was observed, only a small increase in

FO$_2$ radical concentrations was detected, and the concentration of O$_3$ was unchanged, allowing the uppper limit to k tabulated above to be derived.

Preferred Values

$k < 1 \times 10^{-14}$ cm^3 molecule^{-1}s^{-1} at 298 K.

Comments on Preferred Values

The recommended upper limit to the rate coefficient is based on the results of Li et al.[2] A much higher upper limit was reported by Sehested et al.[1] A much lower upper limit was derived by Colussi and Grela[3] from a reanalysis of data

that had been reported by Staricco et al.[4] for ozone destruction quantum yields in the F$_2$-photosensitized decomposition of ozone. Results of the recent, more direct study of Li et al.[2] are preferred over the much earlier results reported by Staricco et al.[4]

References

[1] J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, J. Phys. Chem. **98**, 6731 (1994).
[2] Z. Li, R. R. Friedl, and S. P. Sander, J. Phys. Chem. **99**, 13445 (1995).
[3] A. J. Colussi and M. A. Grela, Chem. Phys. Lett. **229**, 134 (1994).
[4] E. H. Staricco, J. E. Sicre, and H. J. Schumacher, Z. Phys. Chem. N.F. **31**, 385 (1962).

FO+NO→F+NO$_2$

$\Delta H° = -87$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.6 \pm 0.5) \times 10^{-11}$	298	Ray and Watson, 1981[1]	DF-MS
$1.86 \times 10^{-11}(T/300)^{-(0.66 \pm 0.13)}$	300–845	Bedzhanyan, Markin, and Gershenzon, 1993[2]	DF-LMR
$(1.9 \pm 0.4) \times 10^{-11}$	300		

Preferred Values

$k = 2.2 \times 10^{-11}$ cm^3 molecule^{-1}s^{-1} at 298 K.
$k = 8.2 \times 10^{-12}$ exp(300/T) cm^3 molecule^{-1}s^{-1} over the temperature range 290–850 K.

Reliability
$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values
The preferred room temperature value is the average of the

room temperature values from the only two studies of Ray and Watson[1] and Bedzhanyan et al.[2] The temperature dependence is derived from a fit to the data of Bedzhanyan et al.[2] and the A factor is fitted to the preferred 298 K value. The temperature dependence is similar to those for the analogous ClO and BrO radical reactions.

References

[1] G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 2955 (1981).
[2] Yu. R. Bedzhanyan, E. M. Markin, and Yu. M. Gershenzon, Kinet. Catal. **34**, 1 (1993); original pages 7–10 (1993).

$$FO+FO \rightarrow 2F+O_2 \quad (1)$$

$$\rightarrow FO_2+F \quad (2)$$

$$\rightarrow F_2+O_2 \quad (3)$$
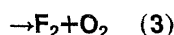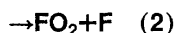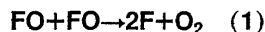
$\Delta H°(1) = -59 \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta H°(2) = -113 \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta H°(3) = -218 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data ($k=k_1+k_2+k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.5\pm2.8)\times10^{-12}$	298	Clyne and Watson, 1974[1]	DF-MS
$1.0\times10^{-11} (T/300)^{0.85\pm0.5}$	300–435	Bedzhanyan, Markin, and Gershenzon, 1993[2]	DF-LMR

Preferred Values

$k = 1.0\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 290–440 K.

Reliability

$\Delta \log k = \pm0.2$ at 298 K.
$\Delta(E/R) = \pm250 \text{ K}$.

Comments on Preferred Values

The recommended value is based on the results of Clyne and Watson[1] and Bedzhanyan et al.[2] In a less direct study, Wagner et al.[3] reported a factor of 3 higher value. Although

Bedzhanyan et al.[2] reported a weak temperature dependence, a temperature-independent rate coefficient fits their data equally well and is recommended in this evaluation. The study of Bedzhanyan et al.[2] showed that the predominant reaction channel is that to produce $2F+O_2$.

References

[1] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 **70**, 1109 (1974).

[2] Yu. R. Bedzhanyan, E. M. Markin, and Yu. M. Gershenzon, Kinet. Catal. **33**, 601 (1993); original pages 753–759 (1992).

[3] H. Gg. Wagner, C. Zetzsch, and J. Warnatz, Ber. Bunsenges. Phys. Chem. **76**, 526 (1972).

$FO_2+O_3 \rightarrow$ products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<3.4\times10^{-16}$	298	Sehested et al., 1994[1]	PR-UVA (a)
$<3\times10^{-15}$	298	Li, Friedl, and Sander, 1995[2]	DF-MS (b)

Comments

(a) Pulse radiolysis of O_3–O_2–SF_6 mixtures in a high pressure cell at 18 bar of SF_6. The decay of FO_2 radicals was monitored in absorption at 220 nm.

(b) First-order decay rate of FO_2 in presence of excess O_3 at 1.3 mbar (1 Torr) total pressure was monitored by mass spectrometry.

Preferred Values

$k < 4\times10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

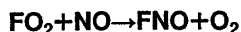The preferred room temperature upper limit to the rate coefficient is based on results of the pulse radiolysis-UV absorption study of Sehested et al.[1] A higher upper limit was reported by Li et al.[2]

References

[1] J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, J. Phys. Chem. **98**, 6731 (1994).

[2] Z. Li, R. R. Friedl, and S. P. Sander, J. Phys. Chem. **99**, 13445 (1995).

$FO_2+NO\rightarrow FNO+O_2$

$\Delta H^\circ = -182\,kJ\cdot mol^{-1}$

Rate coefficient data

$k/cm^3\,molecule^{-1}\,s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.5\pm0.1)\times10^{-12}$	298	Sehested et al., 1994[1]	PR-UVA (a)
$7.5\times10^{-12}\exp[-(688\pm377)/T]$	190–298	Li, Friedl, and Sander, 1995[2]	DF-MS (b)
$(8.5\pm1.3)\times10^{-13}$	298		

Comments

(a) Pulse radiolysis of $NO-O_2-SF_6$ mixtures in a low pressure cell at 1 bar SF_6. The formation of FNO was monitored in absorption at 310.5 nm. The yield of FNO was determined to be $(100\pm14)\%$.

(b) First-order decay rates of FO_2 in the presence of excess NO at 1.3 mbar (1 Torr) total pressure were monitored by mass spectrometry. The yield of FNO was concluded to be nearly 100%.

Preferred Values

$k=7.5\times10^{-13}\,cm^3\,molecule^{-1}\,s^{-1}$ at 298 K.

$k=7.5\times10^{-12}\exp(-690/T)cm^3\,molecule^{-1}\,s^{-1}$ over the temperature range 190–300 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm400$ K.

Comments on Preferred Values

The preferred values are based on results of the temperature-dependent study of Li et al.[2] The higher room temperature rate coefficient of Sehested et al.[1] is encompassed within the assigned uncertainty limits.

References

[1] J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, J. Phys. Chem. **98**, 6731 (1994).

[2] Z. Li, R. R. Friedl, and S. P. Sander, J. Phys. Chem. **99**, 13445 (1995).

$FO_2+NO_2\rightarrow products$
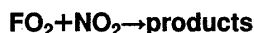
Rate coefficient data

$k/cm^3\,molecule^{-1}\,s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.05\pm0.15)\times10^{-13}$	298	Sehested et al., 1994[1]	PR-UVA (a)
$3.8\times10^{-11}\exp[-(2042\pm456)/T]$	260–315	Li, Friedl, and Sander, 1995[2]	DF-MS (b)
$(4.2\pm0.8)\times10^{-14}$	298		

Comments

(a) Pulse radiolysis of $NO_2-O_2-SF_6$ mixtures in a low pressure cell at 1 bar SF_6 and also in a high pressure cell at 18 bar SF_6. The decay of NO_2 was monitored in absorption at 400 nm, and that of FO_2 radicals at 220 nm. The rate coefficient showed no dependence on pressure over the pressure range 1–18 bar of SF_6.

(b) First-order decay rate of FO_2 radicals in the presence of excess NO_2 at 1.3 mbar (1 Torr) total pressure was monitored by mass spectrometry.

Preferred Values

$k=4.0\times10^{-14}\,cm^3\,molecule^{-1}\,s^{-1}$ at 298 K.

$k=3.8\times10^{-11}\exp(-2040/T)\,cm^3\,molecule^{-1}\,s^{-1}$ over the temperature range 260–320 K.

Reliability

$\Delta\log k=\pm0.3$ at 298 K.

$\Delta(E/R)=\pm500$ K.

Comments on Preferred Values

The preferred values are based on results of the temperature-dependent study of Li et al.[2] The higher room

temperature result of Sehested *et al.*[1] might be attributable to a small NO impurity in the NO_2 sample used. The observed positive temperature dependence suggests that reaction occurs primarily by a simple bimolecular mechanism yielding $FNO_2 + O_2$.

References

[1]J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, J. Phys. Chem. **98**, 6731 (1994).
[2]Z. Li. R. R. Friedl, and S. P. Sander, J. Phys. Chem. **99**, 13445 (1995).

$FO_2 + CO \rightarrow$ products

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<5.1 \times 10^{-16}$	298	Sehested *et al.*, 1994[1]	PR-UVA (a)

Comments

(a) Pulse radiolysis of $CO-O_2-SF_6$ mixtures in a high pressure cell at 18 bar SF_6. The decay of FO_2 radicals was monitored in absorption at 220 nm.

Preferred Values

$k < 6 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

Comments on Preferred Values

The preferred room temperature upper limit is based on results of the pulse radiolysis-UV absorption study of Sehested *et al.*[1] This is the sole reported study of this reaction.

References

[1]J. Sehested, K. Sehested, O. J. Nielsen, and T. J. Wallington, J. Phys. Chem. **98**, 6731 (1994).

4.2. Chlorine Species

$O + HOCl \rightarrow HO + ClO$

$\Delta H° = -30 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

k/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.2) \times 10^{-13}$	298	Vogt and Schindler, 1992[1]	DF-MS
$(1.7 \pm 0.3) \times 10^{-13}$	213–298	Schindler, Dethlefs, and Schmidt, 1996[2]	DF-MS

Preferred Values

$k = 1.7 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, independent of temperature over the range 210–300 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are based on the results of the study of Schindler *et al.*,[2] in which k was found to be independent of temperature over the range 213–298 K. These results are preferred over those of the previous study[1] from the same laboratory, which was only at room temperature. In the most recent study,[2] product analysis using ^{18}O atoms and *ab initio* model calculations indicate that Cl atom abstraction is the predominant primary reaction channel.
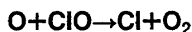
References

[1]R. Vogt and R. N. Schindler, Geophys. Res. Lett. **19**, 1935 (1992).
[2]R. N. Schindler, J. Dethlefs, and M. Schmidt, Ber. Bunsenges. Phys. Chem. **100**, 1242 (1996).

O+ClO→Cl+O$_2$

$\Delta H^\circ = -229.5 \, \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.3\pm0.8)\times10^{-11}$	298	Bemand, Clyne, and Watson, 1973[1]	DF-RF
$(5.7\pm2.3)\times10^{-11}$	298	Bemand, Clyne, and Watson, 1973[1]	DF-MS
$1.07\times10^{-10}\exp[-(224\pm76)/T]$	220–426	Clyne and Nip, 1976[2]	DF-RF
$(5.2\pm1.6)\times10^{-11}$	298		
$5.2\times10^{-11}\exp[-(96\pm20)/T]$	236–422	Leu, 1984[3]	DF-RF
$(3.6\pm0.7)\times10^{-11}$	296		
$(4.2\pm0.8)\times10^{-11}$	241–298	Margitan. 1984[4]	PLP-RF
$(3.5\pm0.5)\times10^{-11}$	252–347	Schwab *et al.*, 1984[5]	DF-RF/RA/LMR (a)
$1.55\times10^{-11}\exp[(263\pm60)/T]$	231–367	Nicovich, Wine, and Ravishankara, 1988[6]	PLP-RF (b)
$(3.8\pm0.6)\times10^{-11}$	298		
Relative Rate Coefficients			
$4.5\times10^{-11}\exp[-(14\pm120)/T]$	218–295	Zahniser and Kaufman, 1977[7]	RR (c)
$(4.3\pm0.7)\times10^{-11}$	295		
$2.6\times10^{-11}\exp[(97\pm64)/T]$	220–387	Ongstad and Birks, 1986[8]	RR (d)
$(3.8\pm0.6)\times10^{-11}$	298		

Comments

(a) Discharge flow system with LMR detection of ClO radicals and resonance fluorescence detection of O(^{3}P) and Cl atoms. Pseudofirst order decay of O(^{3}P) atoms in the presence of excess ClO and decay of ClO in the presence of excess O(^{3}P) gave good agreement for the rate coefficent k. There was no discernable temperature dependence over the range studied. The total pressure was in the range 1.1–2.7 mbar.

(b) Dual pulsed laser photolysis system with resonance fluorescence detection in slow flow reactor. ClO radicals were produced by reaction of excess Cl, produced by 351 nm excimer laser photolysis of Cl$_2$, with known concentrations of O$_3$. O(^{3}P) atoms were produced by 266 nm laser photolysis of ClO after appropriate delay time, and were monitored by resonance fluorescence. The measured O(^{3}P) atom decay rate was corrected for losses due to reaction with Cl$_2$ and other routes. The total pressure was in the range 33–667 mbar, and no effect of pressure on the rate coefficient k was observed.

(c) The rate coefficient k was measured relative to k(Cl+O$_3$) using the discharge flow technique in conjunction with resonance fluorescence monitoring of Cl atom concentrations and resonance absorption monitoring of O(^{3}P) atom concentrations in a system where O(^{3}P), Cl, ClO, and O$_3$ had reached a steady-state condition. The tabulated Arrhenius expression was obtained by combining the experimentally determined ratio of k(O+ClO)/k(Cl+O$_3$) = 1.55 exp[(246±30)/T] with the rate coefficient of k(Cl+O$_3$) = 2.9 ×10^{-11}exp(−260/T) cm^3 molecule^{-1} s^{-1} (this evaluation).

(d) Discharge flow system with detection of O(^{3}P) atoms by O+NO+M chemiluminescence in the presence of excess ClO. The ClO radical concentrations were determined indirectly by *in situ* conversion to NO$_2$ by addition of NO and k measured relative to k(O+NO$_2$→NO+O$_2$) = 6.58 × 10^{-12}exp[(142±23)/ T] cm^3 molecule^{-1} s^{-1}, determined concurrently in the same system. The total pressure was 3.1 mbar. No effect of O$_2$ was observed at 230 K.

Preferred Values

$k = 3.8\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 210–430 K.

Reliability
$\Delta \log k = \pm0.1$ at 298 K.
$\Delta(E/R) = \pm250$ K.

Comments on Preferred Values

The most recent studies all give values of k(298 K) about 30% lower than the earlier work of Bemand *et al.*[1] and Clyne and Nip.[2] The two most recent studies[6,8] give a negative temperature dependence, in contrast to the earlier work which showed zero or positive temperature coefficients. The preferred value is independent of temperature and is obtained by averaging the 298 K values from Leu,[3] Margitan,[4] Schwab *et al.*,[5] Nicovich *et al.*,[6] Zahniser and Kaufman,[7] and Ongstad and Birks.[8] The uncertainty on E/R allows for a temperature dependence consistent with all studies. Leu and Yung[9] have shown that the yields of O$_2$($^1\Delta$) and O$_2$($^1\Sigma$) in the reaction are $<2.5\times10^{-2}$ and $(4.4\pm1.1)\times10^{-4}$, respectively.

References

[1]P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 **69**, 1356 (1973).

[2]M. A. A. Clyne and W. S. Nip, J. Chem. Soc. Faraday Trans. 1 **72**, 2211 (1976).

[3]M.-T. Leu, J. Phys. Chem. **88**, 1394 (1984).

[4]J. J. Margitan, J. Phys. Chem. **88**, 3638 (1984).

[5]J. J. Schwab, D. W. Toohey, W. H. Brune, and J. G. Anderson, J. Geophys. Res. **89**, 9581 (1984).

[6]J. M. Nicovich, P. H. Wine, and A. R. Ravishankara, J. Chem. Phys. **89**, 5670 (1988).

[7]M. S. Zahniser and F. Kaufman, J. Chem. Phys. **66**, 3673 (1977).

[8]A. P. Ongstad and J. W. Birks, J. Chem. Phys. **85**, 3359 (1986).

[9]M.-T. Leu and Y. L. Yung, Geophys. Res. Lett. **14**, 949 (1987).

$O + OClO \rightarrow O_2 + ClO$
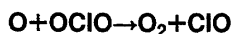
$\Delta H^\circ = -243.2 \, kJ \cdot mol^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5 \pm 2) \times 10^{-13}$	298	Bemand, Clyne, and Watson, 1973[1]	DF-RF/MS (a)
$(1.6 \pm 0.4) \times 10^{-13}$	298	Colussi, 1990[2]	PLP-RF (b)
See Comment	248–312	Colussi, Sander, and Friedl, 1992[3]	PLP-RF (c)
$2.4 \times 10^{-12} \exp[-(960 \pm 120)/T]$	243–400	Gleason. Nesbitt and Stief. 1994[4]	DF-RF (d)
$(1.0 \pm 0.3) \times 10^{-13}$	298		

Comments

(a) Discharge flow system. Two independent methods were used: $O(^3P)$ atom decay in excess OClO monitored by resonance fluorescence, and OClO decay in excess $O(^3P)$ determined by MS. There was only fair agreement between the two methods.

(b) Pulsed laser photolysis of OClO at 308 nm, with the $O(^3P)$ atom decay being determined by resonance fluorescence. The results were extrapolated to zero laser pulse intensity. Measurements were made over the pressure range 13–1040 mbar of Ar. The observed rate coefficients were pressure dependent, indicating the presence of a termolecular association reaction. The value reported for the bimolecular component was not directly measured but was derived from fitting a falloff curve to the experimental data over the entire pressure range.

(c) Pulsed laser photolysis of OClO at 308 nm, with the $O(^3P)$ atom decay being determined by resonance fluorescence. The observed rate coefficients were pressure dependent, indicating the presence of a termolecular association reaction. A negative temperature dependence was observed for the bimolecular component, with the reported values of k increasing from 1.5 $\times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 312 K to 4.0 $\times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 248 K. These values for the bimolecular component were not directly measured but were derived quantities which are consistent with falloff curves fitted to the experimental data over the pressure range 26–800 mbar of Ar.

(d) Discharge flow system with resonance fluorescence detection of $O(^3P)$ atoms. The total pressure was 1–7 mbar. Measurements were made over the temperature range 200–400 K. The data for the temperature range 243–400 K were fitted with the Arrhenius expression given in the table. Data at lower temperatures showed a negative temperature dependence.

Preferred Values

$k = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.4 \times 10^{-12} \exp(-960/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are based on the results of the discharge flow-resonance fluorescence study of Gleason *et al.*[4] Over the temperature range of the recommendation (240–400 K), their data[4] were well fit by the Arrhenius expression given, but at lower temperatures down to 200 K there was an abrupt change to a negative temperature dependence.[4] It appears that the experiments of Bemand *et al.*[1] were complicated by secondary chemistry. The experiments of Colussi[2] and Colussi *et al.*[3] over an extended pressure range demonstrate the importance of the termolecular reaction (see separate data sheet on $O + OClO + M$). However, the extrapolated low pressure rate coefficients of Colussi[2] and Colussi *et al.*[3] show a negative temperature dependence over the range

248–312 K, in contrast to the data of Gleason *et al.*[4] Mauldin *et al.*[5] have studied the mechanism and products of this system at 260 K and a total pressure of 430 mbar of N_2. Under these conditions the value of the rate coefficient for the reaction $O+OClO \rightarrow$ products was reported to be 1.9×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[5] Combining this overall rate coefficient with the observation that the yield of ClO radicals under these conditions is $<5\%$,[5] leads to an upper limit of $k(O+OClO \rightarrow O_2+ClO)$ $<1 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 260 K. This upper limit to the rate coefficient is consistent with the value of Gleason *et al.*,[4] but not with the extrapolated values of Colussi *et al.*[3]

References

[1] P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 **69**, 1356 (1973).

[2] A. J. Colussi, J. Phys. Chem. **94**, 8922 (1990).

[3] A. J. Colussi, S. P. Sander, and R. R. Friedl, J. Phys. Chem. **96**, 4442 (1992).

[4] J. F. Gleason, F. L. Nesbitt, and L. J. Stief, J. Phys. Chem. **98**, 126 (1994).

[5] R. L. Mauldin III, J. B. Burkholder, and A. R. Ravishankara, Int. J. Chem. Kinet. **29**, 139 (1997).

$O+OClO+M \rightarrow ClO_3+M$

$\Delta H^\circ = -112.2$ $kJ \cdot mol^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0 /cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.4 \pm 0.3) \times 10^{-31}$ [Ar]	298	Colussi, 1990[1]	PLP-RF (a)
1.8×10^{-31} $(T/298)^{-1}$ [Ar]	248–312	Colussi, Sander, and Friedl, 1992[2]	PLP-RF (b)

Comments

(a) Pulsed laser photolysis of OClO at pressures of Ar between 10 and 1000 mbar. The oxygen atoms produced were detected by resonance fluorescence. Fit of the falloff curve used $F_c = 0.6$.

(b) See comment (a). The falloff curves were fitted with $F_c = 0.5$ at 248 K, 0.48 at 273 K, and 0.45 at 312 K.

Preferred Values

$k_0 = 1.8 \times 10^{-31}$ $(T/298)^{-1}$ $[N_2]$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 240–320 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$ K.

Comments on Preferred Values

The preferred values are based on the data of Colussi *et al.*[2] using falloff extrapolations with a fitted value of $F_c = 0.47$ at 298 K. A representation of F_c in the form $F_c = \exp(-T/T^*)$ leads to $T^* = 400$ K.

High-pressure rate coefficients

Rate coefficient data

k_∞ /cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.1 \pm 0.8) \times 10^{-11}$	298	Colussi, 1990[1]	PLP-RF (a)
3.1×10^{-11} $(T/298)^1$	248–312	Colussi, Sander, and Friedl, 1992[2]	PLP-RF (b)

Comments

(a) See comment (a) for k_0.
(b) See comment (b) for k_0.

Preferred Values

$k_\infty = 3.1 \times 10^{-11} (T/298)^1$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–320 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

See comments on k_0. The rate coefficients of Colussi *et al.*[2] were confirmed by measurements carried out by Mauldin *et al.*[3] at 260 K and 430 mbar of N$_2$. Under these conditions (260 K and 430 mbar of N$_2$), Mauldin *et al.*[3] observed that the reaction led to the formation of ClO radicals with a yield of $<5\%$. Mauldin *et al.*[3] concluded that the combination reaction may involve the intermediate formation of a species such as O·OClO which is different from ClO$_3$ and which does not rearrange to give O$_2$+ClO.

References

[1] A. J. Colussi, J. Phys. Chem. **94**, 8922 (1990).
[2] A. J. Colussi, S. P. Sander, and R. R. Friedl, J. Phys. Chem. **96**, 4442 (1992).
[3] R. L. Mauldin III, J. B. Burkholder, and A. R. Ravishankara, Int. J. Chem. Kinet. **29**, 139 (1997).

O+Cl$_2$O→ClO+ClO
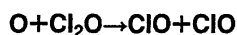
$\Delta H° = -123.1$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.7 \times 10^{-11} \exp[-(560 \pm 80)/T]$	236–295	Miziolek and Molina, 1978[1]	DF-CL
$(4.1 \pm 0.5) \times 10^{-12}$	295		
$3.3 \times 10^{-11} \exp[-(700 \pm 150)/T]$	237–297	Wecker, Johanssen, and Schindler, 1982[2]	DF-EPR
$(3.1 \pm 0.5) \times 10^{-12}$	297		
$2.7 \times 10^{-11} \exp[-(510 \pm 30)/T]$	230–380	Stevens and Anderson, 1992[3]	DF-RF
$(4.7 \pm 0.2) \times 10^{-12}$	298		

Preferred Values

$k = 4.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.7 \times 10^{-11} \exp(-530/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–380 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred value at 298 K is based on the results of Stevens and Anderson[3] and Miziolek and Molina,[1] which are in good agreement. The significantly lower values of Wecker *et al.*[2] are not included, nor are earlier, higher results of Basco and Dogra[4] and Freeman and Phillips[5] due to data analysis difficulties in both studies.[4,5]

References

[1] A. W. Miziolek and M. J. Molina, J. Phys. Chem. **82**, 1769 (1978).
[2] D. Wecker, R. Johanssen, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **86**, 532 (1982).
[3] P. S. Stevens and J. G. Anderson, J. Phys. Chem. **96**, 1708 (1992).
[4] N. Basco and S. K. Dogra, Proc. Roy. Soc. London A **323**, 29 (1971).
[5] C. G. Freeman and L. F. Phillips, J. Phys. Chem. **72**, 3025 (1968).

$$O + ClONO_2 \rightarrow ClO + NO_3 \quad (1)$$

$$\rightarrow OClO + NO_2 \quad (2)$$

$$\rightarrow O_2 + ClONO \quad (3)$$
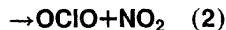
$\Delta H^\circ(1) = -96.7 \, \text{kJ} \cdot \text{mol}^{-1}$
$\Delta H^\circ(2) = -143.3 \, \text{kJ} \cdot \text{mol}^{-1}$
$\Delta H^\circ(3) = -216 \, \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.0 \pm 0.2) \times 10^{-13}$	245	Ravishankara et al., 1977[1]	FP-RF
$3.4 \times 10^{-12} \exp[-(840 \pm 60)/T]$	213–295	Molina, Spencer, and Molina, 1977[2]	DF-CL
$(2.0 \pm 0.4) \times 10^{-13}$	295		
$1.9 \times 10^{-12} \exp[-(692 \pm 167)/T]$	225–273	Kurylo, 1977[3]	FP-RF
1.8×10^{-13}	298*		
$(2.3 \pm 0.6) \times 10^{-13}$	298	Adler-Golden and Wiesenfeld, 1981[4]	FP-RA
$(2.4 \pm 0.4) \times 10^{-13}$	298	Tyndall et al., 1997[5]	PLP-RF
$4.5 \times 10^{-12} \exp[-(900 \pm 80)/T]$	202–325	Goldfarb et al., 1998[6]	PLP-RF/A (a)
$(2.2 \pm 0.2) \times 10^{-13}$	298		

Comments

(a) k was measured by two independent techniques: (1) pulsed laser photolysis with time-resolved resonance fluorescence detection of O-atom decay, and (2) pulsed laser photolysis with time-resolved long-path absorption at 662 nm by the product NO_3 radical. The yield of NO_3 radicals produced in the reaction was also measured in the long-path absorption apparatus.

Preferred Values

$k = 2.2 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 4.5 \times 10^{-12} \exp(-900/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–330 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 150$ K.

*Comments on Preferred Values*

The preferred values are based on the results of the study of Goldfarb et al.[6] This study encompassed the broadest range of experimental conditions and used two completely different techniques. Results obtained by these two techniques were in complete agreement. Results of the earlier temperature dependent studies of Molina et al.[2] and Kurylo[3] and the room temperature studies of Adler-Golden and Wiesenfeld[4] and Tyndall et al.[5] are in good agreement with the preferred values.

Using the long-path absorption apparatus to monitor NO_3 radicals, Goldfarb et al.[6] measured the yield of the NO_3 radical produced in this reaction to be approximately unity. Allowing for uncertainties in the measurements they concluded that NO_3 and ClO radicals are the primary products of this reaction and account for at least 70% of the reaction over the temperature range studied (248–298 K).[6]

References

[1] A. R. Ravishankara, D. D. Davis, G. Smith, G. Tesi, and J. Spencer, Geophys. Res. Lett. **4**, 7 (1977).

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[5] G. S. Tyndall, C. S. Kegley-Owen, J. J. Orlando, and J. G. Calvert, J. Chem. Soc. Faraday Trans. **93**, 2675 (1997).

[6] L. Goldfarb, M. H. Howard, J. B. Burkholder, and A. R. Ravishankara, J. Phys. Chem. A **102**, 8556 (1998).

$$Cl+H_2 \rightarrow HCl+H$$
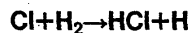
$\Delta H° = 4.4\,kJ\cdot mol^{-1}$

Rate coefficient data

$k/cm^3\,molecule^{-1}\,s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.0\times10^{-11}\exp[-(2164\pm101)/T]$	251–456	Westenberg and de Haas, 1968[1]	DF-EPR
$(1.35\pm0.07)\times10^{-14}$	297		
$(1.26\pm0.1)\times10^{-14}$	298	Davis, Braun, and Bass, 1970[2]	FP-RF (a)
$5.5\times10^{-11}\exp[-(2391\pm50)/T]$	213–350	Watson *et al.*, 1975[3]	FP-RF
$(1.80\pm0.2)\times10^{-14}$	298		
$2.66\times10^{-11}\exp[-(2230\pm60)/T]$	200–500	Lee *et al.*, 1977[4]	FP-RF
$(1.77\pm0.13)\times10^{-14}$	302		
$3.65\times10^{-11}\exp[-(2310\pm20)/T]$	202–498	Miller and Gordon, 1981[5]	FP-RF
$(1.49\pm0.07)\times10^{-14}$	298		
$6.00\times10^{-11}\exp[-(2470\pm100)/T]$	297–425	Kita and Stedman, 1982[6]	DF-RF
$(1.46\pm0.22)\times10^{-14}$	297		
$4.4\times10^{-11}\exp(-2568/T)$	291–1283	Adusei and Fontijn, 1994[7]	FP/PLP-RF
8.1×10^{-15}	291		
$(1.68\pm0.22)\times10^{-14}$	296	Kumaran, Lim, and Michael, 1994[8]	PLP-RA (b)

Comments

(a) Rate coefficient has been decreased by 10%, as recommended by the NASA evaluation panel.[9]

(b) Rate coefficients also measured over the temperature range 699–3020 K, and a combination of the 296 and 699 K to 3020 K rate coefficients resulted in $k=4.78\times10^{-16}T^{1.58}\exp(-1610/T)\,cm^3\,molecule^{-1}\,s^{-1}$.

Preferred Values

$k=1.7\times10^{-14}\,cm^3\,molecule^{-1}\,s^{-1}$ at 298 K.

$k=3.9\times10^{-11}\exp(-2310/T)\,cm^3\,molecule^{-1}\,s^{-1}$ over the temperature range 200–310 K.

Reliability

$\Delta \log k=\pm0.1$ at 298 K.

$\Delta(E/R)=\pm200\,K$.

Comments on Preferred Values

The preferred value is derived from a least-squares fit to the rate coefficients measured at $\leqslant302\,K$ by Watson *et al.*,[3] Lee *et al.*,[4] Miller and Gordon,[5] Kita and Stedman,[6] and Ku-

maran *et al.*[8] The results of these studies are in excellent agreement below $\sim300\,K$; at higher temperatures the data are in poorer agreement. The two studies of Miller and Gordon[5] and Kita and Stedman[6] have measured both the forward and reverse rates and have shown that the rate coefficient ratio agrees with equilibrium constant data. The room temperature rate coefficients of Adusei and Fontijn[7] are in reasonable agreement with the preferred values.

References

[1] A. A. Westenberg and N. de Haas, J. Chem. Phys. 48, 4405 (1968).
[2] D. D. Davis, W. Braun, and A. M. Bass, Int. J. Chem. Kinet. 2, 101 (1970).
[3] R. T. Watson, E. S. Machado, R. L. Schiff, S. Fischer, and D. D. Davis, Proceedings of the 4th CIAP Conference, DOT-OST-75, 1975.
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[5] J. C. Miller and R. J. Gordon, J. Chem. Phys. 75, 5305 (1991).
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[7] G. Adusei and A. Fontijn, 25th International Symposium on Combustion, 1994 (the Combustion Institute, Pittsburgh, PA, 1994), pp. 801–808.
[8] S. S. Kumaran, K. P. Lim, and J. V. Michael, J. Chem. Phys. 101, 9487 (1994).
[9] NASA Evaluation No. 12, 1997 (see references in Introduction).

$$Cl+HO_2 \rightarrow HCl+O_2 \quad (1)$$

$$\rightarrow ClO+HO \quad (2)$$
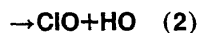
$\Delta H°(1) = -228.2 \text{ kJ} \cdot \text{mol}^{-1}$

$\Delta H°(2) = -5.0 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.23 \pm 0.07) \times 10^{-11}$	250–414	Lee and Howard, 1982[1]	DF-LMR (a)
$k_1 = (4.4 \pm 1.5) \times 10^{-11}$	308	Cattell and Cox, 1986[2]	MM (b)
$k_2 = (9.4 \pm 1.9) \times 10^{-12}$	308		
Branching Ratios			
$k_2/k = 1.09 \exp(-478/T)$	250–414	Lee and Howard, 1982[1]	DF-LMR (a)

Comments

(a) On the basis of the temperature independent overall rate coefficient and the temperature dependent branching ratio, the authors derived the rate coefficient expressions $k_1 = 1.8 \times 10^{-11} \exp[(170 \pm 80)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ and $k_2 = 4.1 \times 10^{-11} \exp[-(450 \pm 60)T]$ $\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$.

(b) Rate coefficients were derived from the observed time-concentration behavior of HO_2 and ClO radicals using computer simulations and a 25-step reaction mechanism. Because of uncertainties in the Cl atom concentrations, the rate coefficients k_1 and k_2 cited above (for 1 bar total pressure) may be low by a factor of 2 and high by a factor of 2, respectively.[2] The reaction was also studied over the pressure range 67–1013 mbar, and no pressure dependence of either k_1 or k_2 over this range was evident.

Preferred Values

$k_1 = 3.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ at 298 K.

$k_2 = 9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ at 298 K.

$k_1 = 1.8 \times 10^{-11} \exp(170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ over the temperature range 250–420 K.

$k_2 = 4.1 \times 10^{-11} \exp(-450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ over the temperature range 250–420 K.

Reliability

$\Delta \log k_1 = \pm 0.2$ at 298 K.

$\Delta \log k_2 = \pm 0.3$ at 298 K.

$\Delta(E_1/R) = \Delta(E_2/R) = \pm 250 \text{ K}.$

Comments on Preferred Values

The preferred values for k_1 and k_2 are based on results of the direct study by Lee and Howard.[1] These expressions were derived by the authors from data on the overall rate coefficient and the branching ratio. The total rate coefficient is temperature independent over the range 250–420 K with a value of $4.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$, and the room temperature results of Cattell and Cox[2] are in good agreement with this recommendation. Based on the combined results of these two studies, neither channel shows any pressure dependence between 1 mbar and 1 bar showing that stabilization of the HOOCl* intermediate does not occur, the two bimolecular channels making up the entire reaction pathway. The more recent study of Dobis and Benson[3] reports a total rate coefficient in good agreement with this recommendation but a significantly lower value of the branching ratio k_2/k. Results of earlier indirect studies[4–7] were not used in the evaluation of the Preferred Values.

References

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[2] F. C. Cattell and R. A. Cox, J. Chem. Soc. Faraday Trans. 2 **82**, 1413 (1986).

[3] O. Dobis and S. W. Benson, J. Am. Chem. Soc. **115**, 8798 (1993).

[4] M.-T. Leu and W. B. DeMore, Chem. Phys. Lett. **41**, 121 (1976).

[5] G. Poulet, G. Le Bras, and J. Combourieu, J. Chem. Phys. **69**, 767 (1978).

[6] J. P. Burrows, D. I. Cliff, G. W. Harris, B. A. Thrush, and J. P. T. Wilkinson, Proc. Roy. Soc. (London) A **368**, 463 (1979).

[7] R. A. Cox, Int. J. Chem. Kinet. **12**, 649 (1980).

$Cl + H_2O_2 \rightarrow HCl + HO_2$
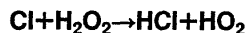
$\Delta H° = -62.7 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.8^{+5.8}_{-2.9}) \times 10^{-13}$	298	Watson *et al.*, 1976[1]	FP-RF (a)
$(6.2 \pm 1.5) \times 10^{-13}$	295	Leu and DeMore, 1976[2]	DF-MS
$1.24 \times 10^{-12} \exp[-(384 \pm 168)/T]$	265–400	Michael *et al.*, 1977[3]	FP-RF (b)
$(3.64 \pm 0.52) \times 10^{-13}$	299		
$(4.0 \pm 0.4) \times 10^{-13}$	298	Poulet, Le Bras, and Combourieu, 1978[4]	DF-MS
$1.05 \times 10^{-11} \exp[-(982 \pm 102)/T]$	298–424	Keyser, 1980[5]	DF-RF
$(4.1 \pm 0.2) \times 10^{-13}$	298		

Comments

(a) A recalculated rate coefficient of $(5.2^{+5.2}_{-2.6}) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is cited in Michael *et al.*[3]

(b) Obtained using H_2O_2 concentrations measured after the reaction cell. Using an average of the H_2O_2 concentrations measured in the reactant flow prior to and after the reaction cell, a rate coefficient of $k = (3.14 \pm 0.56) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 265–400 K, was obtained.

Preferred Values

$k = 4.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.1 \times 10^{-11} \exp(-980/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–430 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The room temperature rate coefficients measured by Watson *et al.*,[1] Leu and DeMore,[2] Michael *et al.*,[3] Poulet *et al.*,[4] and Keyser[5] range from $(3.6–6.2) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The studies of Michael *et al.*,[3] Poulet *et al.*,[4] and Keyser[5] are considered to be the most reliable. The recommended Arrhenius expression is that reported by Keyser.[5] The rate coefficient measured by Michael *et al.*[3] at 265 K is in good agreement with the recommendation; however, the *A* factor reported is considerably lower than that expected from theoretical considerations and may be attributed to decomposition of H_2O_2 above 300 K (which was indeed observed, especially at 400 K). More data are required before the Arrhenius parameters can be considered to be well established. Heneghan and Benson,[6] using mass spectrometry, confirmed that this reaction proceeds only by the H-atom abstraction mechanism.

References

[1] R. Watson, G. Machado, S. Fischer, and D. D. Davis, J. Chem. Phys. **65**, 2126 (1976).

[2] M.-T. Leu and W. B. DeMore, Chem. Phys. Lett. **41**, 121 (1976).

[3] J. V. Michael, D. A. Whytock, J. H. Lee, W. A. Payne, and L. J. Stief, J. Chem. Phys. **67**, 3533 (1977).

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[6] S. P. Heneghan and S. W. Benson, Int. J. Chem. Kinet. **15**, 1311 (1983).
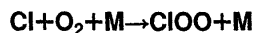
$Cl+O_2+M\rightarrow ClOO+M$

$\Delta H^\circ = -23.8\,kJ\cdot mol^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
5.6×10^{-34}[Ar]	200–300	Clyne and Coxon, 1968[1]	DF (a)
1.7×10^{-33}[N$_2$+O$_2$]	300	Nicholas and Norrish, 1968[2]	FP-UVA (b)
$(8.9\pm2.9)\times10^{-33}$[O$_2$]	186.5	Nicovich et al., 1991[3]	PLP-RF (c)
$1.6\times10^{-33}(T/300)^{-2.9}$[O$_2$]	160–260	Baer et al., 1991[4]	PLP-UVA (d)
$(6.3\pm1.2)\times10^{-33}$[O$_2$]	186.5		
$1.4\times10^{-33}(T/300)^{-3.9}$[N$_2$]	160–260	Baer et al., 1991[4]	PLP-UVA (d)

Comments

(a) Measurements attributed to D. H. Stedman. Cl atoms were monitored by chlorine afterglow emission.

(b) Rate coefficients were determined by a complex analysis of the time-resolved production of ClO radicals in the photolysis of Cl$_2$–O$_2$ mixtures. ClO radicals were measured by photographic recording of their absorption.

(c) Photolysis of Cl$_2$–O$_2$ mixtures at 181–200 K and with O$_2$ pressures of 20–53 mbar. Detection of Cl(^{2}P$_{3/2}$) atoms. An equilibrium constant for the reaction of $K_p=18.9\,bar^{-1}$ was determined at 185.4 K.

(d) Photolysis of Cl$_2$–O$_2$–M mixtures with M=He, Ar, O$_2$ and N$_2$, with detection of ClOO radicals. Redetermination of the ClOO radical absorption cross sections gave $\sigma(248\,nm)=3.4\times10^{-17}\,cm^2$ molecule^{-1}. Measurements over the temperature range 160–260 K and the pressure range 1–1000 bar were in agreement with the data of Mauldin et al.[5] Negligible deviations from third-order behavior were observed at pressures below 10 bar. At higher pressures, an anomalous transition to a high pressure plateau was observed. This and the anomalously strong temperature dependence suggest a radical-complex mechanism. An equilibrium constant of $K_p=5.3\times10^{-6}\,exp(23.4\,kJ\,mol^{-1}/RT)\,bar^{-1}$ was determined over the temperature range 180–300 K.

Preferred Values

$k_0=1.4\times10^{-33}\,(T/300)^{-3.9}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 160–300 K.

$k_0=1.6\times10^{-33}\,(T/300)^{-2.9}$ [O$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 160–300 K.

Reliability

$\Delta\log k_0=\pm0.2$ at 200 K.

$\Delta n=\pm1$.

Comments on Preferred Values

The two recent studies of Nicovich et al.[3] and Baer et al.[4] are in good agreement and are also consistent with the older data of Nicholas and Norrish,[2] if one takes into account the strong temperature dependence of k_0. The most extensive measurements of Baer et al.[4] are the basis for the preferred values. No falloff expressions are reported here, because deviations from third-order behavior become apparent only at pressures higher than 10 bar and because the falloff formalism does not apply to the radical-complex mechanism operating in this case.

References

[1] M. A. A. Clyne and J. A. Coxon, Proc. Roy. Soc. London A **303**, 207 (1968).

[2] J. E. Nicholas and R. G. W. Norrish, Proc. Roy. Soc. London A **307**, 391 (1968).

[3] J. M. Nicovich, K. D. Kreutter, C. J. Shackelford, and P. H. Wine, Chem. Phys. Lett. **179**, 367 (1991).

[4] S. Baer, H. Hippler, R. Rahn, M. Siefke, N. Seitzinger, and J. Troe, J. Chem. Phys. **95**, 6463 (1991).

[5] R. L. Mauldin III, J. B. Burkholder, and A. R. Ravishankara, J. Phys. Chem. **96**, 2582 (1992).
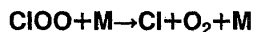
$$\text{ClOO+M}\rightarrow\text{Cl+O}_2\text{+M}$$

$\Delta H^\circ = 23.8\ \text{kJ}\cdot\text{mol}^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.9\times10^{-14}[\text{O}_2]$	185.4	Nicovich *et al.*, 1991[1]	PLP-RF (a)
$2.8\times10^{-10}\exp(-1820/T)\ [\text{N}_2]$	160–260	Baer *et al.*, 1991[2]	PLP-UVA (a)
$6.2\times10^{-13}\ [\text{N}_2]$	298*		
$6.3\times10^{-10}\exp(-2030/T)\ [\text{O}_2]$	160–260	Baer *et al.*, 1991[2]	PLP-UVA (a)
$1.1\times10^{-14}\ [\text{O}_2]$	185.4		

Comments

(a) From measurements of the reverse reaction and the equilibrium constant.

Preferred Values

$k_0 = 6.2\times10^{-13}\ [\text{N}_2]\,\text{s}^{-1}$ at 298 K.

$k_0 = 2.8\times10^{-10}\exp(-1820/T)\ [\text{N}_2]\,\text{s}^{-1}$ over the temperature range 160–300 K.

Reliability

$\Delta\log k_0 = \pm0.3$ at 298 K.

$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

The preferred values are based on the extensive data of Baer *et al.*[2] No deviations from third-order behavior were observed at pressures below 1 bar. The reaction probably does not proceed via an energy-transfer mechanism (see comments on the reverse reaction Cl+O$_2$+M→ClOO+M), but rather by a radical-complex mechanism.

References

[1] J. M. Nicovich, K. D. Kreutter, C. J. Shackelford, and P. H. Wine, Chem. Phys. Lett. **179**, 367 (1991).
[2] S. Baer, H. Hippler, R. Rahn, M. Siefke, N. Seitzinger, and J. Troe, J. Chem. Phys. **95**, 6463 (1991).

$$\text{Cl+CO+M}\rightarrow\text{ClCO+M}$$

$\Delta H^\circ = -32.6\ \text{kJ}\cdot\text{mol}^{-1}$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.1\pm3.0)\times10^{-34}\ [\text{Ar}]$	300	Clark, Clyne, and Stedman, 1966[1]	DF (a)
$1.05\times10^{-34}\exp[(810\pm70)/T]\ [\text{N}_2]$	185–260	Nicovich, Kreutter, and Wine, 1990[2]	PLP-RF (b)

Comments

(a) Cl atoms were generated from the photolysis of Cl$_2$–He mixtures and were measured by titration with nitrosyl chloride using the red chlorine afterglow spectrum. The total pressure was 2.7–5.3 mbar. From addi-

tional experiments carried out at 195 K, an activation energy of about $-8.4\ \text{kJ mol}^{-1}$ was obtained.

(b) Pulsed laser photolysis of Cl$_2$–CO–M (M=N$_2$, CO, Ar and CO$_2$) mixtures at 355 nm. The total pressure was 19–267 mbar. By second- and third-law analyses of the temperature dependence of the equilibrium constant, a value of $\Delta H^\circ(298\ \text{K}) = -(32.2\pm2.5)\ \text{kJ mol}^{-1}$ was

derived. The relative collision efficiencies were $\beta_c(CO_2):\beta_c(CO/N_2):\beta_c(Ar)=3.2:1.0:0.8$.

Preferred Values

$k_0=1.3\times10^{-33}(T/300)^{-3.8}[N_2]\,cm^3\,molecule^{-1}\,s^{-1}$ over the temperature range 180–300 K.

Reliability

$\Delta\log k_0=\pm0.3$ at 298 K.
$\Delta n=\pm1$.

Comments on Preferred Values

The recommended rate coefficients are based on the measurements of Nicovich et al.[2] At room temperature the preferred value is a factor of two greater than that determined by Clark et al.[1]

References

[1] T. C. Clark, M. A. A. Clyne, and D. H. Stedman, Trans. Faraday Soc. **62**, 3354 (1966).
[2] J. M. Nicovich, K. D. Kreutter, and P. H. Wine, J. Chem. Phys. **92**, 3539 (1990).

$CICO+M\rightarrow CI+CO+M$

$\Delta H^\circ=32.6\,kJ\cdot mol^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.1\times10^{-10}\exp[-(2960\pm160)/T][N_2]$	185–260	Nicovich, Kreutter, and Wine, 1990[1]	PLP-RF (a)

Comments

(a) Pulsed laser photolysis of Cl_2–CO–M (M=N_2, CO, Ar and CO_2) mixtures at 355 nm. The total pressure was 19–267 mbar. By second- and third-law analyses of the temperature dependence of the equilibrium constant, a value of $\Delta H^\circ(298\,K)=(32.2\pm2.5)\,kJ\,mol^{-1}$ was derived. The relative collision efficiencies were $\beta_c(CO_2):\beta_c(CO/N_2):\beta_c(Ar)=3.2:1.0:0.8$.

Preferred Values

$k_0=2.0\times10^{-14}[N_2]\,s^{-1}$ at 298 K.
$k_0=4.1\times10^{-10}\exp(-2960/T)[N_2]\,s^{-1}$ over the temperature range 180–300 K.
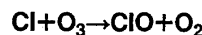
Reliability

$\Delta\log k_0=\pm0.4$ at 298 K.
$\Delta(E/R)=\pm200\,K$.

Comments on Preferred Values

The preferred rate coefficients are based on the study of Nicovich et al.[1]

References

[1] J. M. Nicovich, K. D. Kreutter, and P. H. Wine, J. Chem. Phys. **92**, 3539 (1990).

$$Cl+O_3 \rightarrow ClO+O_2$$

$\Delta H^\circ = -162.4 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$3.08 \times 10^{-11} \exp[-(290 \pm 25)/T]$	220–350	Watson *et al.*, 1976[1]	FP-RF
$(1.20 \pm 0.10) \times 10^{-11}$	298		
$2.17 \times 10^{-11} \exp[-(171 \pm 30)/T]$	205–366	Zahniser, Kaufman, and Anderson, 1976[2]	DF-RF (a)
$(1.23 \pm 0.25) \times 10^{-11}$	298		
$2.72 \times 10^{-11} \exp[-(298 \pm 39)/T]$	213–298	Kurylo and Braun, 1976[3]	FP-RF (a)
$(1.02 \pm 0.15) \times 10^{-11}$	298		
$5.18 \times 10^{-11} \exp[-(418 \pm 28)/T]$	221–629	Clyne and Nip, 1976[4]	DF-RF
$(1.33 \pm 0.26) \times 10^{-11}$	298		
$(1.3 \pm 0.3) \times 10^{-11}$	295	Leu and DeMore, 1976[5]	DF-MS (b)
$(1.3 \pm 0.2) \times 10^{-11}$	298	Toohey, Brune, and Anderson, 1988[6]	DF-RF
$2.49 \times 10^{-11} \exp[-(233 \pm 46)/T]$	269–385	Nicovich, Kreutter, and Wine, 1990[7]	PLP-RF (c)
$1.19 \times 10^{-11} \exp[-(33 \pm 37)/T]$	189–269		
$(1.14 \pm 0.17) \times 10^{-11}$	298		
$1.59 \times 10^{-11} \exp[-(87 \pm 57)/T]$	206–296	Seeley, Jayne, and Molina, 1996[8]	DF-RF (d)
$(1.21 \pm 0.13) \times 10^{-11}$	295		
Relative Rate Coefficients			
1.17×10^{-11}	197	DeMore, 1991[9]	(e)
1.24×10^{-11}	217		

Comments

(a) The *A* factors tabulated are ~8% lower than those originally reported due to a revision of the value used for the O_3 absorption cross sections.

(b) Discharge flow system with MS detection of O_3.

(c) A change in slope of the Arrhenius plot was observed at ~270 K. The data were fitted to two separate Arrhenius expressions over the temperature ranges 189–269 K and 269–385 K.

(d) Turbulent flow conditions were used with total pressures in the range 66–330 mbar.

(e) Competitive chlorination of O_3–CH_4 mixtures. Cl atoms were produced by the photolysis of Cl_2 at 300–400 nm. The measured rate coefficient ratios $k(Cl+O_3)/k(Cl+CH_4)$ are placed on an absolute basis using a rate coefficient of $k(Cl+CH_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.[10]

Preferred Values

$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at 298 K.

$k = 2.9 \times 10^{-11} \exp(-260/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The majority of the rate coefficients for this reaction have been obtained at temperatures at and below 298 K, and our evaluation is restricted to that temperature regime. The preferred value of k at 298 K is the mean of the absolute room temperature rate coefficients of Watson *et al.*,[1] Zahniser *et al.*,[2] Kurylo and Braun,[3] Clyne and Nip,[4] Leu and DeMore,[5] Toohey *et al.*,[6] Nicovich *et al.*,[7] and Seeley *et al.*,[8] all of which are in excellent agreement. The preferred Arrhenius expression is a least-squares fit to all of the data at and below 298 K from the studies of Watson *et al.*,[1] Zahniser *et al.*,[2] Kurylo and Braun,[3] Clyne and Nip,[4] Leu and DeMore,[5] Toohey *et al.*,[6] Nicovich *et al.*,[7] Seeley *et al.*,[8] and DeMore,[9] with the pre-exponential factor being adjusted to fit the value of k at 298 K.

Nicovich *et al.*[7] observed non-Arrhenius behavior in the temperature range studied (189–385 K). The data of Nicovich *et al.*[7] are in excellent agreement with the present recommendation above ~250 K; at lower temperatures their data are higher than the recommendation although still within the stated uncertainty down to ~220 K.

Vanderzanden and Birks[11] have interpreted their observation of oxygen atoms in this system as evidence for some production (0.1%–0.5%) of $O_2(^1\Sigma_g)$ in this reaction. The possible production of singlet molecular oxygen in this reaction has also been discussed by DeMore[12] in connection with the Cl_2 photosensitized decomposition of ozone. However, Choo and Leu[13] were unable to detect $O_2(^1\Sigma)$ or $O_2(^1\Delta)$ in the $Cl+O_3$ system and set upper limits to the branching ratios for their production of 5×10^{-4} and 2.5×10^{-2}, respec-

tively. A recent crossed molecular beam study[14] also found no evidence for the production of electronically excited O_2. Choo and Leu[13] suggested two possible mechanisms for the observed production of oxygen atoms, involving reactions of vibrationally excited ClO radicals with O_3 or with Cl atoms, respectively. Burkholder et al.[15] in a study of infrared line intensities of the ClO radical present evidence in support of the second mechanism. In their experiments with excess Cl atoms, the vibrationally excited ClO radicals produced in the $Cl+O_3$ reaction can react with Cl atoms to give Cl_2 and oxygen atoms which can then remove additional ClO radicals.[15] These authors[15] point out the possibility for systematic error from assuming a 1:1 stoichiometry for [ClO] : $[O_3]_0$ when using the $Cl+O_3$ reaction as a quantitative source of ClO radicals for kinetic and spectroscopic studies.

References

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$Cl+HONO_2 \rightarrow HCl+NO_3$
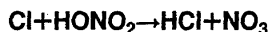
$\Delta H^\circ = -4.8\,kJ\cdot mol^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<5\times10^{-16}$	293	Zagogianni, Mellouki, and Poulet, 1987[1]	DF-EPR
$<2.0\times10^{-16}$	298–400	Wine, Wells, and Nicovich, 1988[2]	PLP-AS/RF (a)

Comments

(a) Pulsed laser photolysis of Cl_2–HNO_3 mixtures at 351 nm. NO_3 radical concentrations were monitored using long-path absorption spectroscopy. Experiments in which Cl atom concentrations were measured by resonance fluorescence were also carried out, but were less sensitive and resulted in higher upper limits to the rate coefficient k.

Preferred Values

$k<2\times10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The preferred upper limit to the rate coefficient is that obtained by Wine et al.,[2] which receives support from the slightly higher value obtained by Zagogianni et al.[1] Values from earlier studies[3–5] are well above the preferred upper limit to the rate coefficient k.

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$$Cl+NO_3 \rightarrow ClO+NO_2$$
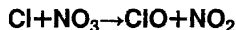
$\Delta H^\circ = -60.2 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.6\pm0.5)\times10^{-11}$	298	Mellouki, Le Bras, and Poulet, 1987[1]	DF-EPR/MS
$(2.26\pm0.17)\times10^{-11}$	298	Becker *et al.*, 1991[2]	DF-MS

Preferred Values

$k = 2.4\times10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 400 \text{ K}$.

Comments on Preferred Values

The preferred value at room temperature is based on the studies of Mellouki *et al.*[1] and Becker *et al.*[2] The results of these direct absolute rate studies are preferred over those of earlier relative rate studies,[3-5] in which NO_3 was monitored in the photolysis of Cl_2–$ClONO_2$–N_2 mixtures. The agree-

ment among these earlier studies[3-5] is not good and probably arises from complications in the chemistry of the systems used. This radical–radical reaction is expected to have a negligible temperature dependence, which is consistent with the results of Cox *et al.*[5] over the temperature range 278–338 K.

References

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$$Cl+OClO \rightarrow ClO+ClO$$
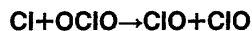
$\Delta H^\circ = -13.6 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$>8.3\times0^{-13}$	298	Clyne and Coxon, 1968[1]	DF-UVA
$(8.5\pm1.2)\times10^{-12}$	~298	Basco and Dogra, 1971[2]	FP-UVA
$(5.9\pm0.9)\times10^{-11}$	298–588	Bemand, Clyne, and Watson, 1973[3]	DF-RF/MS (a)
$3.0\times10^{-11}\exp(174/T)$	229–428	Toohey, 1988[4]	DF-RF (b)
$(5.44\pm0.09)\times10^{-11}$	298		
Relative Rate Coefficients			
$3.7\times10^{-10}\exp[-(3020\pm101)/T]$	338–365	Gritsan, Panfilov, and Sukhanow, 1975[5]	(c)

Comments

(a) Discharge flow system with resonance fluorescence detection of Cl atom decay in excess OClO and MS measurement of OClO decay in excess Cl.

(b) The measured rate coefficients $(\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1})$ were: 229 K, $(6.28\pm0.21)\times10^{-11}$; 247 K, $(6.12\pm0.20)\times10^{-11}$; 268 K, $(5.6\pm0.30)\times10^{-11}$; 298 K, $(5.44\pm0.09)\times10^{-11}$; 367 K, $(4.84\pm0.24)\times10^{-11}$;

and 428 K, $(4.40\pm0.17)\times10^{-11}$. A unit-weighted least-squares analysis of these data, using the Arrhenius expression, leads to $k = 3.0\times10^{-11}\exp(174/T)$ $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

(c) Thermal decomposition of OClO. Complex chemical system.

Preferred Values

$k = 5.7 \times 0^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ at 298 K.

$k = 3.2 \times 10^{-11}\,exp(170/T)\,cm^3\,molecule^{-1}\,s^{-1}$ over the temperature range 220–430 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The data of Toohey[4] agree well with the earlier study of Bemand et al.[3] at 298 K, but show a small negative temperature dependence over a similar temperature range to that over which Bemand et al.[3] saw little change in k. The preferred value is the average of the 298 K values from the two studies

of Bemand et al.[3] and Toohey,[4] and the temperature dependence of Toohey[4] is accepted but with error limits covering the possibility that k is independent of temperature. The earlier data of Clyne and Coxon[1] and Basco and Dogra[2] are rejected following the recommendation of Bemand et al.[3]

References

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[2] N. Basco and S. K. Dogra, Proc. Roy. Soc. (London) A **323**, 417 (1971).
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[4] D. W. Toohey, "Kinetic and Mechanistic Studies of Reactions of Bromine and Chlorine Species Important in the Earth's Stratosphere," Ph.D. thesis, Harvard University, Cambridge, MA, 1988.
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$Cl + Cl_2O \rightarrow Cl_2 + ClO$
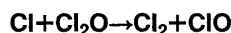
$\Delta H^\circ = -96.9\,kJ \cdot mol^{-1}$

Rate coefficient data

$k/cm^3\,molecule^{-1}\,s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.33 \pm 0.54) \times 10^{-11}$	298	Ray, Keyser, and Watson, 1980[1]	DF-MS
$(1.03 \pm 0.08) \times 10^{-10}$	298	Ray, Keyser, and Watson, 1980[1]	DF-RF
$6.0 \times 10^{-11}\,exp[(127 \pm 30)T]$	233–373	Stevens and Anderson, 1992[2]	DF-RF
$(9.1 \pm 0.4) \times 10^{-11}$	298		

Preferred Values

$k = 9.6 \times 10^{-11}\,cm^3\,molecule^{-1}\,s^{-1}$ at 298 K.

$k = 6.2 \times 10^{-11}\,exp(130/T)\,cm^3\,molecule^{-1}\,s^{-1}$ over the temperature range 230–380 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 130$ K.

Comments on Preferred Values

The preferred room temperature value is the mean of the value reported by Stevens and Anderson[2] and the values obtained by Ray et al.[1] using two completely independent tech-

niques. This value is confirmed by the relative rate study of Burrows and Cox.[3] The much lower value reported earlier by Basco and Dogra[4] has been rejected. The recommended temperature dependence is from Stevens and Anderson.[2] There is apparently no pressure dependence over the range 1 mbar–1 bar.[1–3]

References

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$Cl+Cl_2O_2 \rightarrow Cl_2+ClOO$
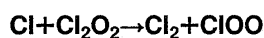
$\Delta H° = -151.4 \, kJ \cdot mol^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.00\pm0.02)\times10^{-10}$	233	Cox and Hayman, 1988[1]	(a)

Comments

(a) Static photolysis of Cl_2–Cl_2O–N_2 mixtures at 350 nm. The time dependence of $[Cl_2O_2]$ and $[Cl_2O]$ were monitored by photodiode array UV spectroscopy, yielding $k(Cl+Cl_2O)/2k=0.54\pm0.01$ at 233 K. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(Cl+Cl_2O)=1.08\times10^{-10}\,cm^3$ molecule^{-1} s^{-1} at 233 K (this evaluation).

Preferred Values

$k=1.0\times10^{-10}\,cm^3$ molecule^{-1}s^{-1}, independent of temperature over the range 230–300 K.

Reliability

$\Delta \log k=\pm0.3$ at 298 K.
$\Delta(E/R)=\pm300$ K.

Comments on Preferred Values

The preferred values are based on the relative rate study of Cox and Hayman,[1] which is supported by the unpublished rate coefficient of Friedl[2] of $(1.0\pm0.4)\times10^{-10}\,cm^3$ molecule^{-1}s^{-1} at 298 K. The agreement of the room temperature value and that at 233 K along with the high value of k precludes a significant temperature dependence.

References

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[2] R. R. Friedl (unpublished data, 1991).

$Cl+ClONO_2 \rightarrow Cl_2+NO_3$
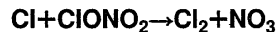
$\Delta H° = -70.5 \, kJ \cdot mol^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$6.3\times10^{-12}\exp(150/T)$	219–298	Margitan, 1983[1]	FP-RF (a)
$(1.04\pm0.04)\times10^{-11}$	298		
$7.3\times10^{-12}\exp(165/T)$	220–296	Kurylo, Knable, and Murphy, 1983[2]	FP-RF (b)
$(1.20\pm0.24)\times10^{-11}$	296		
$6.0\times10^{-12}\exp[(140\pm30)/T]$	195–354	Yokelson *et al.*, 1995[3]	PLP-RF/
$(9.6\pm1.0)\times10^{-12}$	298		TDLS (c)
$(9.1\pm1.2)\times10^{-12}$	298	Tyndall *et al.*, 1997[4]	PLP-RF

Comments

(a) The $O(^3P)$ atom abstraction channel to give $ClO+ClONO$ was shown to be unimportant based on results of experiments with added NO, in which Cl was not regenerated by the fast reaction $ClO+NO \rightarrow Cl+NO_2$.

(b) Supersedes earlier results from the same laboratory.

(c) Decay of Cl atoms measured by RF and formation of NO_3 radicals measured by TDLS.

Preferred Values

$k=1.0\times10^{-11}\,cm^3$ molecule^{-1}s^{-1} at 298 K.
$k=6.5\times10^{-12}\exp(135/T)\,cm^3$ molecule^{-1}s^{-1} over the temperature range 190–360 K.

Reliability

$\Delta \log k=\pm0.10$ at 298 K.
$\Delta(E/R)=\pm50$ K.

Comments on Preferred Values

The recommended Arrhenius equation is derived from the results of Margitan[1] and Yokelson et al.,[3] which are in excellent agreement. The data of Kurylo et al.[2] and Tyndall et al.[4] also fall within the recommended error limits. Margitan[1] has shown that the reaction proceeds by Cl-atom abstraction rather than by O-atom abstraction and this was confirmed by Yokelson et al.,[3] who found that at 298 K more than 95% of the reaction formed Cl_2 and NO_3.

References

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$HO + Cl_2 \rightarrow HOCl + Cl$
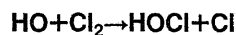
$\Delta H^\circ = 4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.5 \pm 0.3) \times 10^{-14}$	298	Leu and Lin, 1979[1]	DF-RF
$\sim 7.4 \times 10^{-14}$	298	Ravishankara, Eisele, and Wine, 1983[2]	DF-RF
$(6.70 \pm 0.72) \times 10^{-14}$	298 ± 3	Loewenstein and Anderson, 1984[3]	DF-RF
$1.7 \times 10^{-12} \exp[-(911 \pm 373)/T]$	253–333	Boodaghians et al.,1987[4]	DF-RF
$(6.8 \pm 1.0) \times 10^{-14}$	293		
$3.77 \times 10^{-12} \exp[-(1228 \pm 140)/T]$	231–354	Gilles, Burkholder, and Ravishankara, 1999[5]	PLP-LIF
$(5.95 \pm 0.75) \times 10^{-14}$	298		

Preferred Values

$k = 6.5 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 3.6 \times 10^{-12} \exp(-1200/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 230–360 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are based on the data of Loewenstein and Anderson,[3] Boodaghians et al.,[4] and Gilles et al.,[5] which are in good agreement concerning the room temperature rate coefficient. Because of the wider temperature range covered and more extensive study conducted, the temperature dependence is that reported by Gilles et al.[5] with the pre-exponential factor A being adjusted to fit the preferred 298 K rate coefficient. Loewenstein and Anderson[3] determined that the exclusive products are $HOCl + Cl$.

References

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HO+HCl→H$_2$O+Cl

$\Delta H^\circ = -67.5 \, \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.4\pm0.7)\times10^{-13}$	295	Takacs and Glass, 1973[1]	DF-EPR
$4.1\times10^{-12}\exp[-(529\pm24)/T]$	220–480	Smith and Zellner, 1974[2]	FP-RA
$(6.9\pm1)\times10^{-13}$	298		
$2.0\times10^{-12}\exp[-(312\pm10)/T]$	224–440	Zahniser, Kaufman, and Anderson, 1974[3]	DF-RF
$(6.7\pm0.4)\times10^{-13}$	297		
$(6.6\pm1.7)\times10^{-13}$	293	Hack, Mex, and Wagner, 1977[4]	DF-EPR (a)
$3.3\times10^{-12}\exp[-(472\pm40)/T]$	250–402	Ravishankara *et al.*, 1977[5]	FP-RF
$(6.6\pm0.4)\times10^{-13}$	298		
$(6.66\pm0.52)\times10^{-13}$	300	Husain, Plane, and Slater, 1981[6]	FP-RF
$(6.8\pm0.25)\times10^{-13}$	298±4	Cannon, Robertshaw, and Smith, 1984[7]	FP-LIF
$2.1\times10^{-12}\exp[-(285\pm40)/T]$	258–334	Keyser, 1984[8]	DF-RF
$(7.9\pm0.4)\times10^{-13}$	295±2		
$4.6\times10^{-12}\exp[-(500\pm60)/T]$	240–295	Molina, Molina, and Smith, 1984[9]	PLP/FP-RF
$(8.5\pm1.5)\times10^{-13}$	295		
$2.94\times10^{-12}\exp[-(446\pm32)/T]$	300–700	Husain, Plane, and Xiang, 1984[10]	FP-RF
$(6.7\pm0.46)\times10^{-13}$	300		
$2.4\times10^{-12}\exp[-(327\pm28)/T]$	240–363	Ravishankara *et al.*, 1985[11]	FP-RF/
$(8.01\pm0.44)\times10^{-13}$	298		PLP-RF/PLP-LIF (b)
$(7.8\pm0.3)\times10^{-13}$	298	Sharkey and Smith, 1993[12]	PLP-LIF
$(5.4\pm0.25)\times10^{-13}$	216		
$(5.6\pm0.45)\times10^{-13}$	178		
$(5.2\pm0.3)\times10^{-13}$	138		
$3.28\times10^{-17}\,T^{1.66}\exp(184/T)$	200–400	Battin-Leclerc *et al.*, 1999[13]	PLP-LIF (c)
$(7.96\pm0.60)\times10^{-13}$	298		

Comments

(a) Rate coefficients also measured at 435 and 567 K, of 8.1×10^{-13} and 1.25×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively.

(b) Rate coefficients measured over the temperature range 240–1055 K. Arrhenius plot of rate coefficient data over this extended temperature range is curved, with $k=4.5\times10^{-17}\,T^{1.65}\exp(112/T)$ cm^3 molecule^{-1} s^{-1}.

(c) Over the limited temperature range 200–298 K, the data were also fit to the Arrhenius expression, with $k = 1.7\times10^{-12}\exp[-(225\pm20)/T]$ cm^3 molecule^{-1} s^{-1} (note that the publication[13] gives a pre-exponential factor in the Arrhenius expression of 1.7×10^{-11} cm^3 molecule^{-1} s^{-1}). Rate coefficients were also measured for the reactions of the HO radical with DCl (252–387 K) and for the reactions of the DO radical with HCl (213–372 K) and DCl (213–401 K).

Preferred Values

$k = 8.0\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.8\times10^{-12}\exp(-240/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm0.06$ at 298 K.

$\Delta(E/R) = \pm100$ K.

Comments on Preferred Values

The studies of Keyser,[8] Molina *et al.*,[9] Ravishankara *et al.*,[11] and Battin-Leclerc *et al.*,[13] which paid careful attention to the HCl present in the experiments, all show room temperature values higher by about 20%–25% than most other studies.[1-7,10] Ravishankara *et al.*[11] showed that HCl losses can be a problem, leading to erroneously low measured rate coefficients, and this is a plausible cause of these discrepancies. The rate coefficients obtained in the recent and extensive study of Battin-Leclerc *et al.*[13] are in good agreement with the data of Keyser,[8] Molina *et al.*,[9] and Ravishankara *et al.*[11] However, the rate coefficients measured by Battin-Leclerc *et al.*[13] at temperatures <240 K lead to a curved Arrhenius plot, in agreement with the previous study of Ravishankara *et al.*[11] which extended to 1055 K and which also observed non-Arrhenius behavior. The preferred temperature-dependent expression for the range 200–300 K is obtained by a linear least-squares fit to the ≤299 K data from the studies of Keyser,[8] Molina *et al.*,[9] Ravishankara *et al.*,[11] and Battin-Leclerc *et al.*[13] Over more extended temperature ranges the three parameter expression obtained by Battin-Leclerc *et al.*[13] should be used. Results of the low

temperature study of Sharkey and Smith[12] are in good agreement with the recommended Arrhenius expression down to 216 K, but are (as expected due to the non-Arrhenius behavior) significantly higher at 178 and 138 K.

References

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[4] W. Hack, G. Mex, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem. **81**, 677 (1977).

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[6] D. Husain, J. M. C. Plane, and N. K. H. Slater, J. Chem. Soc. Faraday Trans. 2 **77**, 1949 (1981).

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[8] L. F. Keyser, J. Phys. Chem. **88**, 4750 (1984).

[9] M. J. Molina, L. T. Molina, and C. A. Smith, Int. J. Chem. Kinet. **16**, 1151 (1984).

[10] D. Husain, J. M. C. Plane, and C. C. Xiang, J. Chem. Soc. Faraday Trans. 2 **80**, 713 (1984).

[11] A. R. Ravishankara, P. H. Wine, J. R. Wells, and R. L. Thompson, Int. J. Chem. Kinet. **17**, 1281 (1985).

[12] P. Sharkey and I. W. M. Smith, J. Chem. Soc. Faraday Trans. **89**, 631 (1993).

[13] F. Battin-Leclerc, I. K. Kim, R. K. Talukdar, R. W. Portmann, A. R. Ravishankara, R. Steckler, and D. Brown, J. Phys. Chem. A **103**, 3237 (1999).

$HO + HOCl \rightarrow H_2O + ClO$
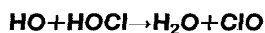
$\Delta H° = -101.5 \, kJ \cdot mol^{-1}$

Rate coefficient data

$k/cm^3 \, molecule^{-1} \, s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.7-9.5) \times 10^{-13}$	298	Ennis and Birks, 1988[1]	DF-RF/MS (a)

Comments

(a) HO radical decays in the presence of excess HOCl were monitored by resonance fluorescence. HOCl concentrations were measured by MS. The effects of the presence of Cl_2O and Cl_2 impurities in the HOCl and the occurrence of secondary reactions were investigated through computer modeling, and the lower and upper limits to the rate coefficient k cited in the table obtained.

Preferred Values

$k = 5.0 \times 10^{-13} \, cm^3 \, molecule^{-1} \, s^{-1}$ at 298 K.

Reliability

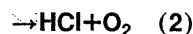$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The only reported experimental value[1] has a large uncertainty, and the preferred value is based on the mid-range value of $5 \times 10^{-13} \, cm^3 \, molecule^{-1} \, s^{-1}$ at 298 K from this study.

References

[1] C. A. Ennis and J. W. Birks, J. Phys. Chem. **92**, 1119 (1988).

$$HO+ClO \rightarrow HO_2+Cl \quad (1)$$

$$\rightarrow HCl+O_2 \quad (2)$$

$\Delta H°(1) = -5.0 \text{ kJ} \cdot \text{mol}^{-1}$

$\Delta H°(2) = -233.2 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.1\pm1.3)\times10^{-12}$	298	Leu and Lin, 1979[1]	DF-RF
$(1.17\pm0.33)\times10^{-11}$	248–335	Ravishankara, Eisele, and Wine, 1983[2]	DF-RF
$(1.19\pm0.09)\times10^{-11}$	243–298	Burrows, Wallington, and Wayne, 1984[3]	DF-RF (a)
$8.0\times10^{-12}\exp[(235\pm46)/T]$	219–373	Hills and Howard, 1984[4]	DF-LMR (b)
$(1.75\pm0.31)\times10^{-11}$	298		
$(1.94\pm0.38)\times10^{-11}$	298	Poulet, Laverdet, and Le Bras, 1986[5]	DF-LIF (c)
$5.5\times10^{-12}\exp[(292\pm72)/T]$	205–298	Lipson *et al.*, 1997[6]	DF-CIMS
$(1.46\pm0.23)\times10^{-11}$	298		
$k_2=1.7\times10^{-13}\exp[(363\pm50)/T]$	210–298	Lipson *et al.*, 1997[6]	DF-CIMS (d)
$k_2=5.7\times10^{-13}$	298		
$8.9\times10^{-12}\exp[(295\pm95)/T]$	234–356	Kegley-Owen *et al.*, 1999[7]	DF (e)
$(2.44\pm0.63)\times10^{-11}$	298		
$k_2=3.2\times10^{-13}\exp[(325\pm60)/T]$	207–298	Lipson *et al.*, 1999[8]	F-CIMS (f)
$k_2=(9.5\pm1.6)\times10^{-13}$	298		
Branching Ratios			
$k_2/k=0.05\pm0.02$	298	Lipson *et al.*, 1997[6]	DF-CIMS (g)
$k_2/k=0.06\pm0.02$	210		

Comments

(a) Rate coefficient ratio of $k_1/k=0.85\pm0.07$, independent of temperature over the range 243–298 K, was determined from measurement of HO_2 radical concentrations (after conversion to HO radicals by reaction with NO).

(b) The rate coefficient ratio, k_1/k, was measured to be $k_1/k=0.86\pm0.14$ at 293 K from measurement of the HO_2 radical concentrations by LMR.

(c) The rate coefficient ratio, k_1/k, was measured to be 0.98 ± 0.12 at 298 K from MS detection of HCl.

(d) Measurements of the DCl product by CIMS in experiments using DO radicals. The overall rate coefficient measured for reaction of DO radicals with ClO radicals was $k=4.2\times10^{-12}\exp[(280\pm114)/T]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–298 K, a factor of 1.35–1.4 lower than the rate coefficient for the HO radical reaction.

(e) HO radicals were generated by pulsed laser photolysis of O_3 (or ClO) at 248 nm and monitored by LIF. ClO radicals were generated by reaction of Cl atoms (produced by a microwave discharge in Cl_2–He mixtures) with O_3, and monitored by UV/visible absorption.

(f) Turbulent flow reactor operated at total pressures of 125–270 mbar. The measurements of the rate coefficients k_2 were combined with the overall rate coefficient $k=5.5\times10^{-12}\exp(292/T)$ cm^3 molecule^{-1} s^{-1} previously determined by the same research group[6] to

derive the branching ratio $k_2/k=0.07\pm0.03$, independent of temperature (207–298 K) and total pressure (125–270 mbar).

(g) From the rate coefficients k_2 and k for the DO radical reaction.

Preferred Values

$k=1.9\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k=7.7\times10^{-12}\exp(270/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–380 K.

$k_2/k=0.07$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm150$ K.

$\Delta(k_2/k)=\pm0.03$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is an average of the rate coefficients of Hills and Howard,[4] Poulet *et al.*[5] Lipson *et al.*,[6] and Kegley-Owen *et al.*[7] The temperature dependence is an average of those obtained by Hills and Howard,[4] Lipson *et al.*,[6] and Kegley-Owen *et al.*,[7] and the preexponential factor A has been adjusted to fit the preferred 298 K rate coefficient. The uncertainties reflect the differ-

ences in the 298 K values and in the reported temperature coefficients. Lipson et al.[8] have measured directly the rate coefficient for the minor channel producing HCl, k_2, and hence obtain the branching ratio k_2/k. This measurement[8] of the branching ratio is preferred, and is in good agreement with the earlier measurement of the branching ratio for HCl formation, k_2/k, based on measurement of the DCl product in the study of the DO+ClO reaction by the same group.[6]

References

[1]M. T. Leu and C. L. Lin, Geophys. Res. Lett. **6**, 425 (1979).
[2]A. R. Ravishankara, F. L. Eisele, and P. H. Wine, J. Chem. Phys. **78**, 1140 (1983).

[3]J. P. Burrows, T. J. Wallington, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **80**, 957 (1984).
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[5]G. Poulet, G. Laverdet, and G. Le Bras, J. Phys. Chem. **90**, 159 (1986).
[6]J. B. Lipson, M. J. Elrod, T. W. Beiderhase, L. T. Molina, and M. J. Molina, J. Chem. Soc. Faraday Trans. **93**, 2665 (1997).
[7]C. S. Kegley-Owen, M. K. Gilles, J. B. Burkholder, and A. R. Ravishankara, J. Phys. Chem. A **103**, 5040 (1999).
[8]J. B. Lipson, T. W. Beiderhase, L. T. Molina, M. J. Molina, and M. Olzmann, J. Phys. Chem. A **103**, 6540 (1999).

$$HO+OClO \rightarrow HOCl+O_2 \quad (1)$$

$$\rightarrow HO_2+ClO \quad (2)$$
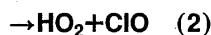
$\Delta H^\circ(1) = -213 \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta H^\circ(2) = -18.7 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
4.50×10^{-13} exp[(804±114)/T]	293–473	Poulet, Zagogianni, and Le Bras, 1986[1]	DF-LIF/EPR (a)
$(7.2 \pm 0.5) \times 10^{-12}$	293		

Comments

(a) HOCl was observed as a reaction product, using MS, and its concentration determined using the HO+Cl$_2$→HOCl+Cl reaction as a calibration source of HOCl. Computer simulation of the reaction system indicated that HOCl is formed primarily in the HO+OClO reaction [channel (1)] and not as a result of secondary reactions of the HO$_2$ radical with ClO, with $k_1/k \geqslant 0.80$ at room temperature.

Preferred Values

$k = 6.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.5 \times 10^{-13}$ exp(800/T) cm^3 molecule^{-1} s^{-1} over the temperature range 290–480 K.
$k_1/k = 1.0$.

Reliability
$\Delta \log k_1 = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 200$ K.
$\Delta(k_1/k) = \pm 0.2$ at 298 K.

Comments on Preferred Values
The preferred values are based on the only experimental study of Poulet et al.,[1] using a discharge flow system with EPR and LIF detection of HO radical decay and molecular beam mass spectrometry detection of the product HOCl. Indication of curvature in the Arrhenius plot dictates caution in extrapolation beyond the experimental range.

References

[1]G. Poulet, H. Zagogianni, and G. Le Bras, Int. J. Chem. Kinet. **18**, 847 (1986).

$$HO+ClNO_2 \rightarrow HOCl+NO_2$$
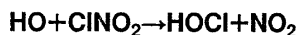
$\Delta H^\circ = -97\,kJ\cdot mol^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.5\pm0.7)\times10^{-14}$	298	Ganske *et al.*, 1991[1]	DF-RF (a)
$2.4\times10^{-12}\exp[-(1250\pm155)/T]$	259–348	Ganske *et al.*, 1992[1]	DF-RF (a)
$(3.6\pm0.2)\times10^{-14}$	298		

Comments

(a) Mass spectrometry showed HOCl to be the sole chlorine-containing product.

Preferred Values

$k=3.6\times10^{-14}$ cm^3 molecule^{-1}s^{-1} at 298 K.

$k=2.4\times10^{-12}\exp(-1250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 260–350 K.

Reliability

$\Delta \log k = \pm0.3$ at 298 K.

$\Delta(E/R) = \pm300$ K.

Comments on Preferred Values

The preferred values are based on the results of the temperature-dependent study of Ganske *et al.*[2] Mass spectrometric measurements[1,2] showed HOCl to be the sole chlorine-containing product, with no evidence for production of HONO$_2$ or Cl$_2$, thereby showing that the only reaction pathway is that yielding HOCl+NO$_2$.

References

[1] J. A. Ganske, M. J. Ezell, H. N. Berko, and B. J. Finlayson-Pitts, Chem. Phys. Lett. **179**, 204 (1991).

[2] J. A. Ganske, H. N. Berko, M. J. Ezell, and B. J. Finlayson-Pitts, J. Phys. Chem. **96**, 2568 (1992).

$$HO+ClONO_2 \rightarrow HOCl+NO_3 \quad (1)$$
$$\rightarrow HO_2+ClONO \quad (2)$$
$$\rightarrow HONO_2+ClO \quad (3)$$
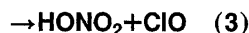
$\Delta H^\circ(1) = -66\,kJ\cdot mol^{-1}$
$\Delta H^\circ(2) = 8\,kJ\cdot mol^{-1}$
$\Delta H^\circ(3) = -95.6\,kJ\cdot mol^{-1}$

Rate coefficient data ($k=k_1+k_2+k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.7\pm0.2)\times10^{-13}$	245	Ravishankara *et al.*, 1977[1]	FP-RF
$1.19\times10^{-12}\exp[-(333\pm22)/T]$	246–387	Zahniser, Chang, and Howard, 1977[2]	DF-RF
$(3.93\pm0.11)\times10^{-13}$	295		

Preferred Values

$k=4.0\times10^{-13}$ cm^3 molecule^{-1}s^{-1} at 298 K.

$k=1.2\times10^{-12}\exp(-330/T)$ cm^3 molecule^{-1}s^{-1} over the temperature range 240–390 K.

Reliability

$\Delta \log k = \pm0.2$ at 298 K.

$\Delta(E/R) = \pm200$ K.

Comments on Preferred Values

The results of the only two reported studies of Ravishan-kara *et al.*[1] and Zahniser *et al.*[2] are in good agreement at 245 K (within 25%), considering the difficulties associated with handling ClONO$_2$. The preferred value is based on the temperature-dependent study of Zahniser *et al.*[2] Neither study reported any data concerning the reaction products.

References

[1] A. R. Ravishankara, D. D. Davis, G. Smith, G. Tesi, and J. Spencer, Geophys. Res. Lett. **4**, 7 (1977).

[2] M. S. Zahniser, J. S. Chang, and F. Kaufman, J. Chem. Phys. **67**, 997 (1977).
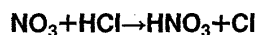
$NO_3+HCl\rightarrow HNO_3+Cl$

$\Delta H^\circ = 4.8\,\text{kJ}\cdot\text{mol}^-$

Rate coefficient data

$k/\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<7\times10^{-18}$	298	Cantrell et al., 1987[1]	(a)
$\leqslant5\times10^{-17}$	298	Mellouki et al., 1989[2]	DF-EPR (b)
$<2.4\times10^{-17}$	298	Canosa-Mas et al., 1989[3]	DF-A (c)

Comments

(a) NO_3 radical concentrations were derived from the measured NO_2 and N_2O_5 concentrations in N_2O_5–NO_2–NO_3–HCl–air mixtures, using the equilibrium constant of Graham and Johnston.[4] The upper limit to the rate coefficient cited above was derived from computer fits of the time-concentration data for reactants and products monitored by FTIR absorption spectrometry.

(b) The upper limit to the rate coefficient cited above was derived from fitting the measured upper limit to the ClO radical concentration (determined by EPR after conversion to Cl atoms) to a complex mechanism.

(c) No reaction was observed at room temperature, leading to the upper limit to the rate coefficient cited above. At higher temperatures (333–473 K), rate coefficients derived from fitting to a complex mechanism yielded the Arrhenius expression of $k=4\times10^{-12}\exp(-3330/T)$ $\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$.

Preferred Values

$k<5\times10^{-17}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ at 298 K.

Comments on Preferred Values

The preferred value is the upper limit to the rate coefficient reported by Mellouki et al.[2] in a study using the discharge flow-EPR technique. Somewhat lower upper limits have been reported by Cantrell et al.[1] and by Canosa-Mas et al.[3] Canosa-Mas et al.[3] also reported Arrhenius parameters at higher temperatures (over the range 333–473 K). The preferred value indicates that this reaction is not important in the chemistry of the atmosphere.

References

[1] C. A. Cantrell, J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert, J. Phys. Chem. **91**, 6017 (1987).

[2] A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, J. Phys. Chem. **93**, 8017 (1989).

[3] C. E. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **85**, 709 (1989).

[4] R. A. Graham and H. S. Johnston, J. Phys. Chem. **82**, 254 (1978).

$$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2 \quad (1)$$

$$\rightarrow \text{HCl} + \text{O}_3 \quad (2)$$
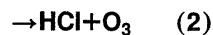
$\Delta H°(1) = -194 \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta H°(2) = -65.8 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.8 \pm 0.7) \times 10^{-12}$	298	Reimann and Kaufman, 1978[1]	DF-RF
$3.3 \times 10^{-11} \exp(-850/T) +$	235–393	Stimpfle, Perry, and Howard, 1979[2]	DF-LMR
$4.5 \times 10^{-12}(T/300)^{-3.7}$			
$(6.43 \pm 0.96) \times 10^{-12}$	298		
$(4.5 \pm 0.9) \times 10^{-12}$	298	Leck, Cook, and Birks, 1980[3]	DF-MS
$(5.4^{+4}_{-2}) \times 10^{-12}$	300	Burrows and Cox, 1981[4]	MM-UVA
$(6.2 \pm 1.5) \times 10^{-12}$	308	Cattell and Cox, 1986[5]	MM-UVA (a)
Branching Ratios			
$k_2/k \leqslant 0.02$	298	Leck, Cook, and Birks, 1980[3]	(b)
$k_2/k \leqslant 0.015$	298	Leu, 1980[6]	(b)
$k_2/k \leqslant 0.03$	248		
$k_2/k \leqslant 0.003$	298	Burrows and Cox, 1981[4]	(c)
$k_1/k > 0.95$	210–300	Finkbeiner *et al.*, 1995[6]	(d)
$k_2/k = 0.05 \pm 0.02$	210		
$k_2/k = 0.02 \pm 0.01$	240		

Comments

(a) k independent of pressure over the range 65–1000 mbar.

(b) DF-MS detection of O_3.

(c) MM-CL detection of O_3.

(d) Flow system with steady-state photolysis (310–400 nm) of Cl_2–H_2–Cl_2O–O_2–Ar mixtures at a total pressure of 910 mbar. HOCl and O_3 products were monitored by matrix-isolation FTIR spectroscopy.

Preferred Values

$k = 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 4.6 \times 10^{-13} \exp(710/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–300 K.

$k_2/k < 0.003$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The data of Cattell and Cox[5] are in good agreement with the earlier measurements,[1–4] and the absence of a pressure dependence excludes a possible addition channel. The lowest upper limit for HCl formation via channel (2) is $k_2 < 2.0 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ at 298 K.[4] The preferred value at room temperature is based on the results reported in Refs. 1–5, and the recommended temperature dependence is calculated from the data of Stimpfle *et al.*[2] over the restricted temperature range 235–298 K (for which the Arrhenius plot was fairly linear).

References

[1] B. Reimann and F. Kaufman, J. Chem. Phys. **69**, 2925 (1978).

[2] R. M. Stimpfle, R. A. Perry, and C. J. Howard, J. Chem. Phys. **71**, 5183 (1979).

[3] T. J. Leck, J.-E. L. Cook, and J. W. Birks, J. Chem. Phys. **72**, 2364 (1980).

[4] J. P. Burrows and R. A. Cox, J. Chem. Soc. Faraday Trans. 1 **77**, 2465 (1981).

[5] F. C. Cattell and R. A. Cox, J. Chem. Soc. Faraday Trans. 2 **82**, 1413 (1986).

[6] M. Finkbeiner, J. N. Crowley, O. Horie, R. Müller, G. K. Moortgat, and P. J. Crutzen, J. Phys. Chem. **99**, 16264 (1995).

$$ClO+O_3 \rightarrow ClOO+O_2 \quad (1)$$

$$\rightarrow OClO+O_2 \quad (2)$$
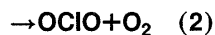
$\Delta H^\circ(1) = -146.9 \, \text{kJ} \cdot \text{mol}^{-1}$
$\Delta H^\circ(2) = -148.7 \, \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data $(k=k_1+k_2)$

$k/\text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_2 < 1 \times 10^{-18}$	298	DeMore, Lin, and Jaffe, 1975[1]	DF-MS
$k_2 < 1 \times 10^{-18}$	298	Wongdontri-Stuper et al., 1979[2]	(a)
$k_1 < 1.3 \times 10^{-17}$	233	Stevens and Anderson, 1990[3]	(b)
$k_1 < 1.4 \times 10^{-17}$	298		
$k_1 = (4.0 \pm 2.0) \times 10^{-16}$	413		

Comments

(a) Flash photolysis of $Cl_2 - O_3$ mixtures. Upper limit to the rate coefficient obtained expected to really refer to k_2.[3]

(b) Discharge flow system. Reaction channel (1) was followed by monitoring ClO produced from the thermal decomposition of the product ClOO in the presence of O_3. The product ClO was distinguished from the reactant ClO through isotopic labeling.

Preferred Values

$k_1 < 1.5 \times 10^{-17} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 298 K.
$k_2 < 1 \times 10^{-18} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 298 K.

Comments on Preferred Values

The preferred upper limit for k_1 is based on the results of the study of Stevens and Anderson.[3] The preferred upper limit for k_2 is based on the data of DeMore et al.[1] and Wongdontri-Stuper et al.[2] The upper limit of Stevens and Anderson[3] at room temperature can be combined with their measured rate coefficient at 413 K to derive $A_1 = 2 \times 10^{-12} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ and $E_1/R > 3600$ K. For k_2 one can estimate $A_2 = 1 \times 10^{-12} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ and derive $E_2/R > 4000$ K.

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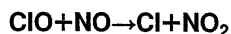[2] W. Wongdontri-Stuper, R. K. M. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **10**, 163 (1979).
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$$ClO+NO \rightarrow Cl+NO_2$$

$\Delta H^\circ = -37.40 \, \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.7 \pm 0.2) \times 10^{-11}$	298	Clyne and Watson, 1974[1]	DF-MS
$5.72 \times 10^{-12} \exp[(296 \pm 20)/T]$	227–415	Leu and DeMore, 1978[2]	DF-MS
$(1.53 \pm 0.11) \times 10^{-11}$	299		
$(1.61 \pm 0.16) \times 10^{-11}$	295	Clyne and MacRobert, 1980[3]	DF-MS
$(1.72 \pm 0.2) \times 10^{-11}$	298	Ray and Watson, 1981[4]	DF-MS
$7.1 \times 10^{-12} \exp[(270 \pm 50)/T]$	202–393	Lee et al., 1982[5]	DF-LMR
$(1.84 \pm 0.03) \times 10^{-11}$	297		

Preferred Values

$k = 1.7 \times 10^{-11} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 298 K.

$k = 6.2 \times 10^{-12} \exp(295/T) \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ over the temperature range 200–420 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The room temperature rate coefficients reported by Clyne and Watson,[1] Leu and DeMore,[2] Clyne and MacRobert,[3] Ray and Watson,[4] and Lee *et al.*[5] are in good agreement and are ~30% lower than the value reported by Zahniser and Kaufman[6] from a competitive study. The preferred values are derived from a least-squares fit to the data reported by Clyne and Watson,[1] Leu and DeMore,[2] Clyne and MacRobert,[3] Ray and Watson,[4] and Lee *et al.*[5]

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$ClO+NO_2+M \rightarrow ClONO_2+M$

$\Delta H^\circ = -111.9 \, kJ \cdot mol^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.3 \times 10^{-33} \exp[(1085 \pm 86)/T][N_2]$	274–339	Cox and Lewis, 1979[1]	(a)
$(1.5 \pm 0.12) \times 10^{-31}[N_2]$	298	Molina, Molina, and Ishiwata, 1980[2]	PLP-UVA (b)
$(1.5 \pm 0.2) \times 10^{-31}[N_2]$	298	Dasch, Sternberg, and Schindler, 1981[3]	PLP-UVA (c)
$2.8 \times 10^{-33} \exp(1090/T)[He]$	250–387	Lee *et al.*, 1982[3]	DF-LMR (d)
$3.5 \times 10^{-33} \exp(1180/T)[O_2]$	250–416		
$2.09 \times 10^{-31}[N_2]$	297		
$(1.8 \pm 0.4) \times 10^{-31}[N_2]$	270–295	Cox, Burrows, and Coker, 1984[5]	(e)
$(1.6 \pm 0.2) \times 10^{-31}(T/300)^{-3.0}[N_2]$	264–343	Handwerk and Zellner, 1984[6]	FP-UVA (f)
$(1.40 \pm 0.07) \times 10^{-31}[N_2]$	298	Wallington and Cox, 1986[7]	(g)
$(1.8 \pm 0.3) \times 10^{-31}(T/300)^{-3.4}$ [air]	213–298	Percival *et al.*, 1997[8]	(h)

Comments

(a) Modulated photolysis with UV absorption detection of ClO radicals. The pressure range studied was 33–815 mbar. Small deviations from third-order kinetics were observed near 1 bar.

(b) The ClO radical decay was monitored. FTIR spectroscopy was also used to monitor the reaction products.

(c) ClO radicals were generated from Cl_2O and monitored at 258.2 nm. The pressure range was 27–800 mbar.

(d) Detection of $ClO(X^2\Pi_{3/2}, v=0)$ with an optically pumped spectrometer. Measurements were carried out at pressures over the range 0.8–8.8 mbar.

(e) Modulated photolysis of Cl_2–Cl_2O–NO_2–N_2 mixtures. $ClONO_2$ formation was followed by diode laser spectroscopy. This study ruled out the formation of isomers other than $ClONO_2$.

(f) The pressure range was 23–1052 mbar, with experiments being conducted at 264, 298, and 343 K.

(g) Modulated photolysis of $OClO$–NO_2–N_2 mixtures with detection of ClO radicals by UV absorption.

(h) Turbulent flow measurements at 213 and 298 K with high pressure chemical ionization mass spectrometry

over the pressure range 200–790 mbar. The falloff extrapolation used $F_c=0.6$, in agreement with earlier data.

Preferred Values

$k_0 = 1.6 \times 10^{-31} (T/300)^{-3.4}[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

There is excellent agreement between the various studies of this reaction in the falloff region close to the low pressure limit.[1-8]

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3-6)\times10^{-12}$	298	Dasch, Sternberg, and Schindler, 1981[3]	PLP-UVA (a)
$(1.2^{+1.2}_{-0.6})\times10^{-11}$	264–343	Handwerk and Zellner, 1984[6]	FP UVA (b)
$(1.5\pm0.7)\times10^{-11}(T/300)^{-1.9}$	213–298	Percival *et al.*, 1997[8]	(c)

Comments

(a) See comment (c) for k_0. The extrapolation to k_∞ is very uncertain, and the value of F_c was unspecified.

(b) See comment (f) for k_0. The extrapolation to k_∞ is very uncertain. The reported value of k_∞ was based on theoretical predictions. Using the reported values of k_0 and k_∞, and $F_c=0.55$, 0.50, and 0.45 at 264, 298, and 343 K, respectively, falloff curves were obtained which are in good agreement with the majority of the available data.

(c) See comment (h) for k_0. The falloff extrapolation was carried out with $F_c=0.6$, independent of temperature.

Preferred Values

$k_\infty=1.5\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–350 K.

Reliability

$\Delta\log k_\infty=\pm0.3$ over the temperature range 250–350 K.

Comments on Preferred Values

Because there are no direct measurements of k at pressures much above 1 bar, k_∞ cannot be established with certainty, and theoretical predictions are no better than within a factor of 2. However, if the falloff curves below 1 bar are fitted with the given values of k_0, k_∞ and F_c, this uncertainty does not influence the representation of the falloff curve in this range. For this reason, we suggest the preferred values with an essentially temperature-independent value of k_∞. We prefer $F_c=0.5$ at 298 K, and representation in the form $F_c=\exp(-T/T^*)$ yields $T^*=430$ K.

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$$\text{ClO}+\text{NO}_3\rightarrow\text{ClOO}+\text{NO}_2 \quad (1)$$
$$\rightarrow\text{OClO}+\text{NO}_2 \quad (2)$$
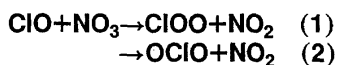
$\Delta H^\circ(1)=-44.7$ kJ$\cdot$mol^{-1}
$\Delta H^\circ(2)=-46.6$ kJ$\cdot$mol^{-1}

Rate coefficient data $(k=k_1+k_2)$

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.0\pm1.6)\times10^{-13}$	296	Cox *et al.*, 1984[1]	MM-A
$1.6\times10^{-12}\exp[-(420\pm200)/T]$	278–338	Cox *et al.*, 1987[2]	MM-A (a)
4.0×10^{-13}	300		
$(5.0\pm1.4)\times10^{-13}$	210–353	Biggs *et al.*, 1991[3]	DF-A/MS (b)
$(4.61\pm0.6)\times10^{-13}$	300	Kukui *et al.*, 1994[4]	DF-MS (c)
$k_2=(1.46\pm0.4)\times10^{-13}$	300		
Branching Ratios			
$k_1/k=0.73$	300	Cox *et al.*, 1987[2]	MM-A (a)
$k_2/k=0.20\pm0.10$	297	Biggs *et al.*, 1991[3]	DF-A/MS (b)

Comments

(a) Derived from computer analysis of the NO_3 radical and ClO radical profiles. At 300 K, $k_1 = (2.9 \pm 0.4) \times 10^{-13}\,cm^3\,molecule^{-1}\,s^{-1}$.

(b) Pseudo-first-order decay of NO_3 in excess ClO was determined by optical absorption at 662 nm, using a cross section of $1.7 \times 10^{-17}\,cm^2\,molecule^{-1}$. Product branching ratios were measured with a quadrupole mass spectrometer. The ratio k_2/k was determined to be 0.20 ± 0.10 at 297 K, decreasing with decreasing temperature to a value of 0.035 ± 0.05 at 216 K.

(c) Rate coefficients k were obtained from the first-order NO_3 radical decays in the presence of excess ClO radicals and O_3. Rate coefficients k_2 were obtained from the decays of ClO radicals in the presence of excess NO_3 radicals, with ClOO radicals formed in channel (1) reforming ClO radicals by the reactions $ClOO \rightarrow Cl + O_2$ and $Cl + NO_3 \rightarrow ClO + NO_2$. This study[4] supersedes the earlier study of Becker *et al.*[5] from the same laboratory.

Preferred Values

$k = 4.6 \times 10^{-13}\,cm^3\,molecule^{-1}\,s^{-1}$, independent of temperature over the range 210–360 K.
$k_2 = 1.2 \times 10^{-13}\,cm^3\,molecule^{-1}\,s^{-1}$ at 298 K.

Reliability
$\Delta \log k = \pm 0.2$ at 298 K.
$\Delta \log k_2 = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 400\,K.$

Comments on Preferred Values

The preferred 298 K value is based on the results of Kukui *et al.*,[4] which are in agreement with the data of Cox *et al.*[1,2] and Biggs *et al.*[3] The results of Cox *et al.*[2] are consistent with those of Biggs *et al.*,[3] who reported that the rate coefficient is independent of temperature over the range 210–353 K. The two direct measurements of the branching ratio k_2/k, of 0.20 ± 0.10 at 297 K[3] and 0.32 ± 0.1 at 300 K,[4] are in agreement that channel (1) dominates, and the preferred value of k_2 is based on the results of these two studies.[3,4] From a study of the $OClO-NO_3$ system, Friedl *et al.*[6] conclude that at 220 and 298 K the major reaction channel is channel (1), in agreement with the conclusions of Cox *et al.*,[2] Biggs *et al.*,[3] and Kukui *et al.*[4] (this latter study superseding the earlier study of Becker *et al.*[5]).

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$$ClO + ClO \rightarrow Cl_2 + O_2 \quad (1)$$
$$\rightarrow Cl + ClOO \quad (2)$$
$$\rightarrow Cl + OClO \quad (3)$$
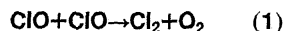
$\Delta H^\circ(1) = -203.2\,kJ\cdot mol^{-1}$
$\Delta H^\circ(2) = 15.6\,kJ\cdot mol^{-1}$
$\Delta H^\circ(3) = 13.7\,kJ\cdot mol^{-1}$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/cm^3\,molecule^{-1}\,s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$k_1 = 1.01 \times 10^{-12} \exp[-(1590 \pm 100)/T]$	260–390	Nickolaisen, Friedl, and Sander, 1994[1]	(a)
$k_2 \sim 2.98 \times 10^{-11} \exp[-(2450 \pm 330)/T]$	260–390		
$k_3 = 3.50 \times 10^{-13} \exp[-(1370 \pm 150)/T]$	260–390		
Branching Ratios			
$k_1/k = 0.39 \pm 0.06$	298	Horowitz, Crowley, and Moortgat, 1994[2]	(b)
$k_2/k = 0.41 \pm 0.06$	298		
$k_3/k = 0.20 \pm 0.03$	298		
$k_3/k_2 = 0.27 \exp[(220 \pm 100)/T]$	285–331		

Comments

(a) Flash photolysis-long pathlength UV absorption technique. Cl_2–Cl_2O mixtures were photolyzed at wavelengths longer than 300 nm. The UV absorption of ClO and OClO were monitored with an optical multichannel analyzer. The reaction was studied over a wide range of temperature, pressure, and initial reactant stoichiometry.

(b) Cl_2-sensitized continuous photolysis of Cl_2–O_3 mixtures in excess O_2. Decay of O_3 and formation of OClO monitored by UV absorption.

Preferred Values

$k_1 = 4.8 \times 10^{-15} \, cm^3 \, molecule^{-1} \, s^{-1}$ at 298 K.
$k_2 = 8.0 \times 10^{-15} \, cm^3 \, molecule^{-1} \, s^{-1}$ at 298 K.
$k_3 = 3.5 \times 10^{-15} \, cm^3 \, molecule^{-1} \, s^{-1}$ at 298 K.
$k_1 = 1.0 \times 10^{-12} \exp(-1590/T) \, cm^3 \, molecule^{-1} \, s^{-1}$ over the temperature range 260–390 K.
$k_2 = 3.0 \times 10^{-11} \exp(-2450/T) \, cm^3 \, molecule^{-1} \, s^{-1}$ over the temperature range 260–390 K.
$k_3 = 3.5 \times 10^{-13} \exp(-1370/T) \, cm^3 \, molecule^{-1} \, s^{-1}$ over the temperature range 260–390 K.

Reliability

$\Delta \log k_1 = \Delta \log k_2 = \Delta \log k_3 = \pm 0.2$ at 298 K.
$\Delta(E_1/R) = \Delta(E_3/R) = \pm 300 \, K.$
$\Delta(E_2/R) = \pm 500 \, K.$

Comments on Preferred Values

The ClO+ClO reaction exhibits both bimolecular and termolecular reaction channels. The termolecular reaction, which leads to the formation of the ClOOCl dimer, dominates at higher pressure (>0.013 bar at 298 K), but is not kinetically important at temperatures above ~283 K because of the instability of the dimer with respect to the reverse decomposition.

The recommended values for the individual reaction channels are those from the study of Nickolaisen et al.[1] This study, using a flash photolysis-long pathlength UV absorp-

tion technique, is the most comprehensive study of this system, covering a wide range of temperature, initial reactant stoichiometry and pressure. These results[1] are preferred over the results of earlier studies of the total bimolecular rate coefficient at low pressures by Clyne and co-workers,[3] as discussed in the reviews of Watson,[4,5] and those of other studies reported by Cox and Derwent,[6] Hayman et al.,[7] Simon et al.,[8] and Horowitz et al.[9]

The room temperature branching ratios from the study of Nickolaisen et al.[1] are $k_1:k_2:k_3 = 0.29:0.50:0.21$. Horowitz et al.[2] in their study of the temperature dependence of the channel branching ratios report slightly different values of $k_1:k_2:k_3 = 0.39:0.41:0.20$ at 298 K and observed distinctly non-Arrhenius behavior for k over the temperature range 285–331 K. Their study[2] was carried out in excess O_2, where the quantum yield for O_3-photosensitized decomposition (which reflects Cl atom generation in this reaction) was consistently lower than in excess N_2. The mechanistic explanation for this observation and for the apparent non-Arrhenius behavior remains obscure. The bath gas effect on $\Phi(-O_3)$ can be accounted for by the observed difference in the branching ratios in the presence of O_2 and N_2, suggesting that O_2 is not involved in the ClO+ClO reaction simply as a third-body quencher.

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$ClO+ClO+M \rightarrow Cl_2O_2+M$

$\Delta H^\circ = -75.7 \, kJ \cdot mol^{-1}$

Low-pressure rate coefficients

Rate coefficient data

$k_0 \, /cm^3 \, molecule^{-1} \, s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.8 \pm 0.5) \times 10^{-32} (T/300)^{-3.6} [N_2]$	194–247	Sander, Friedl, and Yung, 1989[1]	FP-UVA(a)
$(1.64 \pm 0.09) \times 10^{-32} (T/300)^{-4.4} [N_2]$	200–263	Troiler, Mauldin, and Ravishankara, 1990[2]	FP-UVA (b)
$(1.32 \pm 0.08) \times 10^{-32} (T/300)^{-4.4} [O_2]$	200–263		
$1.22 \times 10^{-33} \exp[(833 \pm 34)/T] [N_2]$	195–390	Nickolaisen, Friedl, and Sander, 1994[3]	FP-UVA (c)
$(1.96 \pm 0.24) \times 10^{-32} [N_2]$	300		
$(1.24 \pm 0.09) \times 10^{-32} [O_2]$	300		
$(2.5 \pm 0.4) \times 10^{-32} [N_2]$	300	Bloss, 1999[4]	FP-UVA (d)
$1.7 \times 10^{-32} [N_2]$	300	Stark, 1999[5]	PLP-UVA (e)
$1.1 \times 10^{-31} [N_2]$	200		

Comments

(a) ClO radicals were generated from Cl_2–Cl_2O or Cl_2–O_3 mixtures. The concentrations of the bath gases N_2, Ar or O_2 were in the range of 10^{18}–3 $\times 10^{19}$ molecule cm^{-3}. Falloff extrapolations to k_0 and k_∞ used a value of $F_c = 0.6$.

(b) ClO radicals were generated from Cl_2–O_3 mixtures in the presence of 33–800 mbar of He, N_2, O_2 or SF_6. ClO radicals and Cl_2O_2 were monitored by long-path UV absorption. Falloff curves were extrapolated with $F_c = 0.6$. Difficulties with the simple falloff expression (see Introduction) were encountered.

(c) Pulsed laser photolysis of Cl_2 at $\lambda > 300$ nm in the presence of Cl_2O. ClO radicals were generated by the reaction $Cl + Cl_2O \rightarrow ClO + Cl_2$ and monitored by UV absorption spectroscopy using either a photomultiplier for detection at 275.5 nm or an optical multichannel analyzer for detection over the wavelength range 270–280 nm. Below 250 K, the reaction was in the falloff regime. From a third-law analysis, a value of $\Delta H^\circ = -(75.7 \pm 0.9) \, kJ \, mol^{-1}$ was derived. Third-body efficiencies for the bath gases He, Ar, CF_4, SF_6, and Cl_2 were also determined.

(d) ClO radicals were generated by the flash photolysis of Cl_2–Cl_2O–N_2 mixtures and detected by UV absorption. The bath gas total pressure was varied between 0.25–1 bar. Falloff extrapolation used $F_c = 0.6$. The small discrepancies between the various studies were attributed to the slightly different absorption cross-sections used.

(e) ClO radicals were generated by pulsed laser photolysis of Cl_2O between 0.1 and 1000 bar pressure of He and N_2. The observed pressure dependencies differ from conventional falloff expressions, suggesting overlapping contributions from the energy transfer and radical-complex mechanisms, as well as diffusion control at the highest pressures. The cited rate coefficients apply to a falloff fit for pressures below 1 bar using $F_c = 0.6$.

Preferred Values

$k_0 = 1.7 \times 10^{-32} (T/300)^{-4} [N_2] \, cm^{-3} \, molecule^{-1} \, s^{-1}$ over the temperature range 190–390 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.
$\Delta n = \pm 1.5$.

Comments on Preferred Values

The preferred values are based on the studies of Sander et al.,[1] Troiler et al.,[2] and Nickolaisen et al.[3] The measurements of Bloss[4] and Stark[5] agree with the preferred values within the error limits. Falloff curves below 1 bar pressure are fitted with $F_c = 0.6$.

High-pressure rate coefficients

Rate coefficient data

k_∞ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6\pm2)\times10^{-12}$	194–247	Sander, Friedl, and Yung, 1989[1]	FP-UVA (a)
$(4.8\pm1.3)\times10^{-12}$	200–263	Troiler, Mauldin, and Ravishankara, 1990[2]	FP-UVA (b)
$(6\pm2)\times10^{-12}$	195–390	Nickolaisen, Friedl, and Sander, 1994[3]	FP-UVA (c)
$(5\pm3)\times10^{-12}$	300	Bloss, 1999[4]	FP-UVA (d)
4.5×10^{-12}	300	Stark, 1999[5]	PLP-UVA (e)
7×10^{-12}	200		

Comments

(a)   See comment (a) for k_0.

(b)   See comment (b) for k_0.

(c)   See comment (c) for k_0. The k_∞ value was obtained from falloff data measured below 250 K.

(d)   See comment (d) for k_0.

(e)   See comment (e) for k_0. The cited rate coefficients are given for the energy-transfer mechanism only, such that the falloff curves below 1 bar are fitted. Above 1 bar pressure additional contributions from the radical-complex mechanism become increasingly important such that maximum values of k of 4.5 $\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 300 K and 8 $\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 200 K are reached near 200 bar, before they decrease because of diffusional control.

Preferred Values

$k_\infty=5.4\times10^{-12}$ cm^{-3} molecule^{-1} s^{-1}, independent of temperature over the range 190–390 K.

Reliability

$\Delta \log k_\infty=\pm0.3$ over the temperature range 190–390 K.

Comments on Preferred Values

The preferred values are based on the results of the studies of Sander *et al.*,[1] Troiler *et al.*,[2] and Nickolaisen *et al.*[3] The preferred values should only be used for pressures below 1 bar and with the chosen value of $F_c=0.6$. At higher pressures the combination of the energy transfer, radical-complex and diffusion controlled mechanisms lead to more complicated falloff curves.[5]

References

[1] S. P. Sander, R. R. Friedl, and Y. L. Yung, Science **245**, 1095 (1989).

[2] M. Trolier, R. L. Mauldin III, and A. R. Ravishankara, J. Phys. Chem. **94**, 4896 (1990).

[3] S. L. Nickolaisen, R. R. Friedl, and S. P. Sander, J. Phys. Chem. **98**, 155 (1994).

[4] W. Bloss, Ph.D. thesis, University of Cambridge, Cambridge, UK, 1999.

[5] H. Stark, Ph.D. thesis, University of Göttingen, Göttingen, Germany, 1999.
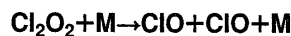
$Cl_2O_2+M\rightarrow ClO+ClO+M$

$\Delta H°=75.7$ kJ · mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0 /s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$9.81\times10^{-7}\exp[-(7980\pm320)/T][N_2]$	260–310	Nickolaisen, Friedl, and Sander, 1994[1]	FP-UVA (a)
$2.30\times10^{-18}[N_2]$	298		

Comments

(a) Photolysis of Cl_2 at $\lambda > 300$ nm in the presence of Cl_2O. ClO radicals were monitored with an optical multichannel analyzer at 270–280 nm. The pressure range used was 33–400 mbar. From a third-law analysis, a value of $\Delta H^\circ = (75.7 \pm 0.9)$ kJ mol^{-1} was derived.

Preferred Values

$k_0 = 2.2 \times 10^{-18} [N_2]$ s^{-1} at 298 K.

$k_0 = 1 \times 10^{-6} \exp(-8000/T)[N_2]$ s^{-1} over the temperature range 260–310 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 900$ K.

Comments on Preferred Values

The preferred values are based on the results of Nickolaisen *et al.*[1]

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.8 \times 10^{15} \exp(-8820/T)$	260–310	Nickolaisen, Friedl, and Sander, 1994[1]	FP-UVA (a)
6.7×10^2	298		

Comments

(a) See comment (a) for k_0. This value is based on the rate coefficient $k_\infty = 6 \times 10^{-12}$ cm^3 molecule^1 s^{-1} for the reverse reaction and the equilibrium constant $K_c = 1.24 \times 10^{-27} \exp(8820/T)$ cm^3 molecule^{-1}, both from Nickolaisen *et al.*[1]

Preferred Values

$k_\infty = 6.7 \times 10^2$ s^{-1} at 298 K.

$k_\infty = 4.8 \times 10^{15} \exp(-8820/T)$ s^{-1} over the temperature range 260–310 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$.

$\Delta(E/R) = \pm 500$ K.

Comments on Preferred Values

The values of Nickolaisen *et al.*[1] are adopted here.

References

[1] S. L. Nickolaisen, R. R. Friedl, and S. P. Sander, J. Phys. Chem. **98**, 155 (1994).

$$ClO + OClO + M \rightarrow Cl_2O_3 + M$$

$\Delta H^\circ = -44$ kJ·mol^{-1}

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.8 \times 10^{-31}[N_2]$	226	Parr *et al.*,1990[1]	MM-UVA (a)
$(6.2 \pm 1.0) \times 10^{-32}(T/300)^{-4.7}[N_2]$	200–260	Burkholder *et al.*,1993[2]	PLP-UVA (b)

Comments

(a) Experiments were carried out with Cl_2–$OClO$–N_2 mixtures in the pressure range 6.4–39 mbar. ClO was monitored at 277.2 nm. The reaction was apparently close to the low pressure limit.

(b) Pulsed laser photolysis of mixtures of N_2O–Cl_2–$OClO$–He or CF_2Cl_2–$OClO$–N_2 at 193 nm. From the first mixture, rate data were obtained while from the second mixture equilibrium constants and the absorption spectra of Cl_2O_3 between 220 and 320 nm were derived. From a second-law analysis of the data, together with those of Hayman and Cox,[3] $\Delta H° = -(46.4 \pm 5.1)$ kJ mol^{-1} and $\Delta S° = -(88.7 \pm 18.9)$ J mol^{-1} K^{-1} were derived. The kinetic data were obtained from a fit of the falloff curves between 33 and 333 mbar total pressure using $F_c = 0.6$

Preferred Values

$k_0 = 6.2 \times 10^{-32}(T/300)^{-4.7}[N_2]$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The values of the extensive study of Burkholder et al.[2] are adopted here. At 226 K the rate coefficient of Parr et al.[1] is in reasonable agreement with our preferred value (and therefore with the data of Burkholder et al.[2]). Recent *ab initio* calculations[4] predict the more stable structure of Cl_2O_3 to be $ClOCl(O)O$ and result in a value of the enthalpy of the recombination reaction of -45.6 kJ mol^{-1}.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.4 \pm 1.2) \times 10^{-11}$	200–260	Burkholder et al., 1993[2]	(a)

Comments

(a) See comment (b) for k_0.

Preferred Values

$k_\infty = 2.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

The preferred values are from Burkholder et al.[2]

References

[1] A. D. Parr, R. P. Wayne, G. D. Hayman, M. E. Jenkin, and R. A. Cox, Geophys. Res. Lett. **17**, 2357 (1990).

[2] J. B. Burkholder, R. L. Mauldin III, R. J. Yokelson, S. Solomon, and A. R. Ravishankara, J. Phys. Chem. **97**, 7597 (1993).

[3] G. D. Hayman and R. A. Cox, Chem. Phys. Lett. **155**, 1 (1989).

[4] J. Clark and J. S. Francisco, J. Phys. Chem. A **101**, 7145 (1997).

$Cl_2O_3+M \rightarrow ClO+OClO+M$

$\Delta H^\circ = 44 \, \text{kJ} \cdot \text{mol}^{-1}$

Low-pressure rate coefficients

No direct measurements are available.

Preferred Values

$k_0 = 2.8 \times 10^{-18} \, [N_2] \, \text{s}^{-1}$ at 226 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 226 K.

Comments on Preferred Values

This value is calculated from the rate coefficient of the reverse reaction, $k_0 = 2.8 \times 10^{-31} \, [N_2] \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 226 K from Parr *et al.*,[1] and the equilibrium constant $K_c = 1.0 \times 10^{-13} \, \text{cm}^3 \, \text{molecule}^{-1}$ at 226 K from Hayman and Cox.[2]

References

[1] A. D. Parr, R. P. Wayne, G. D. Hayman, M. E. Jenkin, and R. A. Cox, Geophys. Res. Lett. **17**, 2357 (1990).
[2] G. D. Hayman and R. A. Cox, Chem. Phys. Lett. **155**, 1 (1989).

$OClO+O_3 \rightarrow ClO_3+O_2$
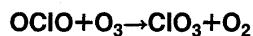
$\Delta H^\circ = -5.7 \, \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.20 \pm 0.15) \times 10^{-19}$	298	Birks *et al.*, 1977[1]	(a)
$2.3 \times 10^{-12} \exp[-(4730 \pm 630)/T]$	262–298	Wongdontri-Stuper *et al.*,1979[2]	(b)
3.0×10^{-19}	298		

Comments

(a) Static system, rate coefficient determined by monitoring the loss of O_3 in excess OClO and also loss of OClO in excess O_3. Both species were measured by UVA; O_3 at 254 nm and OClO at 366 nm.

(b) The decay of OClO in excess O_3 was monitored by UVA at 400 nm. The reaction rate was also determined by the photolysis of Cl_2-O_2 mixtures at 366 nm to produce OClO, followed by monitoring OClO decay in the dark.

Preferred Values

$k = 3.0 \times 10^{-19} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 298 K.

$k = 2.1 \times 10^{-12} \exp(-4700/T) \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ over the temperature range 260–300 K.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K.

$\Delta(E/R) = \pm 1000 \, \text{K}$.

Comments on Preferred Values

The preferred values are based on the results reported in the study of Wongdontri-Stuper *et al.*[2] Within the indicated uncertainty limits, the preferred values encompass the lower room temperature value reported by Birks *et al.*[1]

References

[1] J. W. Birks, B. Shoemaker, T. J. Leck, R. A. Borders, and L. J. Hart, J. Chem. Phys. **66**, 4591 (1977).
[2] W. Wongdontri-Stuper, R. K. M. Jayanty, R. Simonaitis, and J. Heicklen, J. Photochem. **10**, 163 (1979).

$OClO+NO \rightarrow ClO+NO_2$
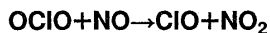
$\Delta H^\circ = -51.0 \, \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.4 \pm 0.5) \times 10^{-13}$	298	Bemand, Clyne, and Watson, 1973[1]	DF-MS

Preferred Values

$k = 3.4 \times 10^{-13} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the only direct study of this reaction reported by Bemand et al.[1] In the absence of experimental data, no recommendation is given for the temperature dependence.

References

[1] P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 **69**, 1356 (1973).

$OClO+NO_3+M \rightarrow O_2ClONO_2+M$
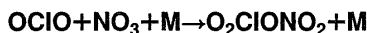
$\Delta H^\circ = -75 \, \text{kJ} \cdot \text{mol}^{-1}$

Low-pressure rate coefficients

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1×10^{-31} [He]	220	Friedl, Sander, and Yung, 1992[1]	(a)

Comments

(a) The experiments were carried out in a long-path absorption flow reactor. NO$_3$ radicals were generated by the reaction of F atoms with HNO$_3$ or of Cl atoms with ClONO$_2$. The products were analyzed by IR and UV absorption measurements. At $T < 230$ K the formation of O$_2$ClONO$_2$ dominated while at higher temperatures ClO and NO$_2$ were also observed, indicating the presence of secondary reactions. The k_0 value was derived from a measured rate coefficient of 2×10^{-14} cm^3 molecule^{-1} s^{-1} at 5 mbar (4 Torr) of He. Using unimolecular rate theory[2] and the experimental parameters, an enthalpy change of $-(75 \pm 13)$ kJ mol^{-1} was derived.

Preferred Values

$k_0 = 1 \times 10^{-31}$[He] cm^3 molecule^{-1} s^{-1} at 220 K.

Reliability

$\Delta \log k_0 = \pm 0.4$ at 220 K.

Comments on Preferred Values

The recommended values are based on the measurements of Friedl et al.[1]

References

[1] R. R. Friedl, S. P. Sander, and Y. L. Yung, J. Phys. Chem. **96**, 7490 (1992).
[2] J. Troe, J. Phys. Chem. **83**, 114 (1979).

$$Cl_2O_2 + O_3 \rightarrow ClO + ClOO + O_2$$

$\Delta H^\circ = -71.2\,\text{kJ}\cdot\text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<1\times10^{-19}$	195–217	DeMore and Tschuikow-Roux, 1990[1]	(a)

Comments

(a) Photolysis ($\lambda > 300\,\text{nm}$) of Cl_2–O_3 or Cl_2–Cl_2O mixtures, both in the gas phase and in the cryogenic solvents CF_4, CO_2 and N_2O. The quantum yield of O_3 loss was measured.

Preferred Values

$k < 1\times10^{-19}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ at 200 K.

Comments on Preferred Values

The recommended upper limit to the rate coefficient is that determined by DeMore and Tschuikow-Roux[1] from measurements of the quantum yield of O_3 loss in the photolysis of Cl_2–O_3 mixtures at $\lambda > 300\,\text{nm}$. The experiments were very sensitive to this reaction. Reaction at a rate greater than this upper limit would have had a marked effect on the quantum yield of ozone loss and also would have resulted in a dependence of the quantum yield on the ozone concentration; however, neither effect was observed.[1] These measurements refer to a temperature of about 200 K; the value of this rate coefficient at higher temperatures would be of no atmospheric significance because of the thermal decomposition of the Cl_2O_2 dimer.

References

[1] W. B. DeMore and E. Tschuikow-Roux, J. Phys. Chem. **94**, 5856 (1990).

4.3. Bromine Species

$$O + HOBr \rightarrow HO + BrO$$
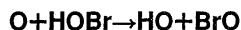
$\Delta H^\circ \le -34\,\text{kJ}\cdot\text{mol}^{-1}$

Rate coefficient data

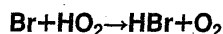| $k/\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.5\pm0.4)\times10^{-11}$	298	Monks *et al.*, 1993[1]	DF-MS
$1.4\times10^{-10}\exp[-(430\pm260)/T]$	233–423	Nesbitt *et al.*, 1995[2]	DF-MS
$(2.5\pm0.6)\times10^{-11}$	298		
$(3.1\pm0.2)\times10^{-11}$	300	Kukui *et al.*, 1996[3]	DF-MS

Preferred Values

$k = 2.8\times10^{-11}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ at 298 K.

$k = 1.2\times10^{-10}\exp(-430/T)\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ over the temperature range 230–430 K.

Reliability

$\Delta \log k = \pm0.2$ at 298 K.

$\Delta(E/R) = \pm300\,\text{K}$.

Comments on Preferred Values

The preferred rate coefficient at 298 K is the mean of the values of Nesbitt *et al.*[2] and Kukui *et al.*,[3] and the temperature dependence is that of Nesbitt *et al.*[2] with the A factor adjusted to yield the preferred rate coefficient at 298 K. Note that the rate coefficient for this reaction is a factor of 200 greater than that for the corresponding reaction of $O(^3P)$ atoms with HOCl (this evaluation).

References

[1] P. S. Monks, F. L. Nesbitt, M. Scanlon, and L. J. Stief, J. Phys. Chem. **97**, 11699 (1993).

[2] F. L. Nesbitt, P. S. Monks, W. A. Payne, and L. J. Stief, Geophys. Res. Lett. **22**, 827 (1995).

[3] A. Kukui, U. Kirchner, Th. Benter, and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **100**, 455 (1996).

$O+BrO \rightarrow O_2+Br$
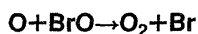
$\Delta H^\circ = -257 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.9 \times 10^{-11} \exp[(230 \pm 150)/T]$	231–328	Thorn *et al.*, 1995[1]	(a)
$(4.1 \pm 0.6) \times 10^{-11}$	298		

Comments

(a) Pulsed laser flash photolysis system with detection of BrO radicals by long path absorption and of $O(^3P)$ atoms by resonance fluorescence.

Preferred Values

$k = 4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ at 298 K.
$k = 1.9 \times 10^{-11} \exp(230/T) \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ over the temperature range 230–330 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 150 \text{ K}$.

Comments on Preferred Values

The preferred value is based on the direct study of Thorn *et al.*,[1] in which the decay of $O(^3P)$ in the presence of excess BrO was monitored. Clyne *et al.*[2] reported an approximately 40% lower room temperature value.

References

[1] R. P. Thorn, J. M. Cronkhite, J. M. Nicovich, and P. H. Wine, J. Chem. Phys. **102**, 4131 (1995).
[2] M. A. A. Clyne, P. B. Monkhouse, and L. W. Townsend, Int. J. Chem. Kinet. **8**, 425 (1976).

$Br+HO_2 \rightarrow HBr+O_2$

$\Delta H^\circ = -162.8 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.4 \times 10^{-11} \exp[-(590 \pm 140)/T]$	260–390	Toohey, Brune, and Anderson, 1987[1]	DF-LMR/RF (a)
$(2.0 \pm 0.3) \times 10^{-12}$	298		
$(1.5 \pm 0.2) \times 10^{-12}$	298	Laverdet *et al.*, 1990[2]	DF-EPR

Comments

(a) k determined from HO_2 decay in the presence of excess Br.

Preferred Values

$k = 2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}$ at 298 K.
$k = 1.4 \times 10^{-11} \exp(-590/T) \text{ molecule}^{-1}\text{s}^{-1}$ over the temperature range 260–390 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

This recommendation is based on results obtained over the 260–390 K temperature range by Toohey *et al.*[1] The value determined by Laverdet *et al.*[2] is in reasonable agreement with this recommendation. Laverdet *et al.*[2] have reinterpreted previous indirect measurements conducted in the same laboratory by Poulet *et al.*[3] to give a range of values higher than had been reported[3] and in agreement with the present recommendation.

References

[1] D. W. Toohey, Wm. H. Brune, and J. G. Anderson, J. Phys. Chem. **91**, 1215 (1987).
[2] G. Laverdet, G. Le Bras, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **172**, 430 (1990).
[3] G. Poulet, G. Laverdet, and G. Le Bras, J. Chem. Phys. **80**, 1922 (1984).

$$Br+H_2O_2 \rightarrow HBr+HO_2 \quad (1)$$

$$\rightarrow HOBr+HO \quad (2)$$
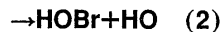
$\Delta H^\circ(1) = 2.8 \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta H^\circ(2) \geqslant 8 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$<5 \times 10^{-16}$	298	Toohey, Brune, and Anderson, 1987[1]	DF-RF (a)
$<5 \times 10^{-16}$	378		

Comments

(a) Decays of Br monitored in the presence of excess H_2O_2. Attempted measurement of HO_2 and HO products by LMR allowed upper limits of $5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ to be derived for either channel (1) or (2).

Preferred Values

$k < 5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ at 298 K.

Comments on Preferred Values

The upper limit to the preferred value is based on the data of Toohey *et al.*,[1] who also obtained the same upper limit at 378 K.

References

[1] D. W. Toohey, Wm. H. Brune, and J. G. Anderson, J. Phys. Chem. **91**, 1215 (1987).

$$Br+O_3 \rightarrow BrO+O_2$$
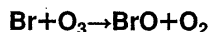
$\Delta H^\circ = -135 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.2) \times 10^{-12}$	298	Clyne and Watson, 1975[1]	DF-MS
$3.34 \times 10^{-11} \exp[-(978 \pm 36)/T]$	224–422	Leu and DeMore, 1977[2]	DF-MS
$(1.16 \pm 0.16) \times 10^{-12}$	298		
$7.74 \times 10^{-12} \exp[-(603 \pm 16)/T]$	200–360	Michael *et al.*, 1978[3]	FP-RF
$(1.01 \pm 0.18) \times 10^{-12}$	298		
$9.45 \times 10^{-12} \exp[-(659 \pm 64)/T]$	234–360	Michael and Payne, 1979[4]	DF-RF
$(1.12 \pm 0.07) \times 10^{-12}$	298		
$3.28 \times 10^{-11} \exp[-(944 \pm 30)/T]$	248–418	Toohey, Brune, and Anderson, 1988[5]	DF-RF
$(1.42 \pm 0.03) \times 10^{-12}$	298		
$1.50 \times 10^{-11} \exp[-(775 \pm 30)/T]$	195–392	Nicovich, Kreutter, and Wine, 1990[6]	LFP-RF
$(1.11 \pm 0.07) \times 10^{-12}$	298		

Preferred Values

$k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ at 298 K.
$k = 1.7 \times 10^{-11} \exp(-800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ over the temperature range 190–430 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The recommended Arrhenius expression is based on a fi to the results of Clyne and Watson,[1] Leu and DeMore, Michael *et al.*,[3] Michael and Payne,[4] Toohey *et al.*,[5] and Nicovich *et al.*[6]

References

[1] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 **71**, 336 (1975).

[2] M. T. Leu and W. B. DeMore, Chem. Phys. Lett. **48**, 317 (1977).

[3] J. V. Michael, J. H. Lee, W. A. Payne, and L. J. Stief, J. Chem. Phys. **68**, 4093 (1978).

[4] J. V. Michael and W. A. Payne, Int. J. Chem. Kinet. **11**, 799 (1979).

[5] D. W. Toohey, W. H. Brune, and J. G. Anderson, Int. J. Chem. Kinet. **20**, 131 (1988).

[6] J. M. Nicovich, K. D. Kreutter, and P. H. Wine, Int. J. Chem. Kinet. **22**, 399 (1990).

$Br+NO_2+M \rightarrow products+M$

Low-pressure rate coefficients

Rate coefficient data

k_0 /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.7\pm0.7)\times10^{-31}$ [He]	298	Mellouki et al., 1989[1]	DF-EPR/MS (a)
$(2.75\pm0.55)\times10^{-31}$ [He]	298	Kreutter, Nicovich, and Wine, 1991[2]	PLP-RF (b)
$4.24\times10^{-31}(T/300)^{-2.4}$ [N$_2$]	259–346		

Comments

(a) Pressure range was between 0.8 and 2.8 mbar.

(b) Pressure range was between 16.7 and 933 mbar, with the bath gases He, Ar, H$_2$, N$_2$, CO$_2$, CF$_4$, and SF$_6$. Falloff curves were analyzed with a theoretically modeled value of F_c=0.59 at 259 K, 0.55 at 298 K, and 0.50 at 346 K.

Preferred Values

$k_0=4.2\times10^{-31}(T/300)^{-2.4}$ [N$_2$] cm^3 molecule^{-1} s^{-1} over the temperature range 250–350 K.

Reliability

$\Delta \log k_0=\pm0.3$ at 298 K.

$\Delta n=\pm1$.

Comments on Preferred Values

The preferred values are based on the results of the study of Kreutter et al.,[2] which are consistent with theoretical predictions. The falloff curves are represented with F_c=0.55 at 298 K.

High-pressure rate coefficients

Rate coefficient data

k_∞ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.66×10^{-11}	259–346	Kreutter, Nicovich, and Wine, 1991[2]	PLP-RF (a)

Comments

(a) See comment (b) for k_0.

Preferred Values

$k_\infty=2.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–350 K.

Reliability

$\Delta \log k_\infty=\pm0.4$ over the range 250–350 K.

Comments on Preferred Values

See comments on k_0. There is only a single determination of k_∞,[2] but the measured falloff curve appears well behaved with rate coefficients close to those of the reactions I+NO+M and I+NO$_2$+M (see this evaluation).

References

[1] A. Mellouki, G. Laverdet, J. L. Jourdain, and G. Poulet, Int. J. Chem. Kinet. **21**, 1161 (1989).

[2] K. D. Kreutter, J. M. Nicovich, and P. H. Wine, J. Phys. Chem. **95**, 402 (1991).

Br+OClO→BrO+ClO

$\Delta H^\circ = 14 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comment
Absolute Rate Coefficients			
4.2×10^{-13}	298	Clyne and Watson, 1977[1]	DF-MS (a)
$2.5 \times 10^{-11} \exp(-1336/T)$	267–423	Toohey, 1988[2]	DF-RF (b)
$(2.82 \pm 0.03) \times 10^{-13}$	299		

Comments

(a) MS detection of OClO in an excess of Br atoms. The observed decays were first order, but computer modeling was used to correct for the effects of the reverse reaction.

(b) The measured rate coefficients (in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ units) were: 267 K, $(1.70 \pm 0.03) \times 10^{-13}$; 294 K, $(2.63 \pm 0.04) \times 10^{-13}$; 299 K, $(2.82 \pm 0.03) \times 10^{-13}$; 325 K, $(4.03 \pm 0.07) \times 10^{-13}$; 351 K, $(5.45 \pm 0.22) \times 10^{-13}$; 385 K, $(7.88 \pm 0.24) \times 10^{-13}$; and 423 K, $(1.06 \pm 0.04) \times 10^{-12}$. A unit-weighted least-squares fit of these data to the Arrhenius expression results in $k = 2.5 \times 10^{-11} \exp(-1336/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ over the temperature range 267–423 K.

Preferred Values

$k = 3.5 \times 10^{-13} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at 298 K.

$k = 2.7 \times 10^{-11} \exp(-1300/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ over the temperature range 260–430 K.
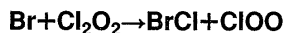
Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred value at 298 K is the mean of the value reported by Clyne and Watson[1] and Toohey.[2] In the former study[1] corrections were made for the effects of the reverse reaction, which was not done in the earlier study by Clyne and Coxon[3] and which is therefore not used in this evaluation. The temperature dependence of k obtained by Toohey is accepted, but with substantial uncertainty limits in the absence of confirmatory studies, and is combined with the preferred value of k at 298 K to obtain the preferred Arrhenius expression.

References

[1] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 **73** 1169 (1977).

[2] D. W. Toohey, "Kinetic and Mechanistic Studies of Reactions of Bromine and Chlorine Species Important in the Earth's Stratosphere," Ph.D thesis, Harvard University, Cambridge, MA, 1988.

[3] M. A. A. Clyne and J. A. Coxon, Proc. Roy. Soc. London A **298**, 42 (1967).

$Br + Cl_2O \rightarrow BrCl + ClO$

$\Delta H^\circ = -72.8 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.1 \times 10^{-11} \exp[-(520 \pm 260)/T]$	220–298	Sander and Friedl, 1989[1]	FP-AS (a)
$(3.79 \pm 0.38) \times 10^{-12}$	298		
$2.1 \times 10^{-11} \exp[-(435 \pm 30)/T]$	233–402	Stevens and Anderson, 1992[2]	DF-RF
$(4.8 \pm 0.2) \times 10^{-12}$	298		

Comments

(a)   Flash photolysis ($\lambda > 300$ nm) of Br_2 in the presence of an excess of Cl_2O at 130 mbar pressure of Ar. ClO radical concentrations were monitored by long-path UV absorption at 275.2 nm.

Preferred Values

$k = 4.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.1 \times 10^{-11} \exp(-470/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–410 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The studies of Sander and Friedl[1] and Stevens and Anderson,[2] which used totally different techniques, are in good agreement. The preferred values are based on the results of these two studies.[1,2] The significantly lower value (by a factor of 4) reported earlier by Basco and Dogra[3] is not used in the evaluation. In the same study, Basco and Dogra[3] reported a value for $k(Cl + Cl_2O)$ more than two orders of magnitude less than that recommended in the present evaluation, suggesting errors in their method of determining the ClO radical concentration which was used to monitor the progress of the reaction.

References

[1] S. P. Sander and R. R. Friedl, J. Phys. Chem. **93**, 4764 (1989).
[2] P. S. Stevens and J. G. Anderson, J. Phys. Chem. **96**, 1708 (1992).
[3] N. Basco and S. K. Dogra, Proc. Roy. Soc. London A **323**, 401 (1971).

$Br + Cl_2O_2 \rightarrow BrCl + ClOO$

$\Delta H^\circ = -127.4 \text{ kJ} \cdot \text{mol}^{-1}$

There are no published measurements of this rate coefficient

Preferred Values

$k = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the results of an unpublished discharge flow study of R. R. Friedl (1991). Substantial uncertainties are suggested in the absence of confirmatory studies.

HO+HBr→H$_2$O+Br
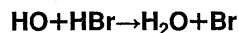
$\Delta H° = -133.0 \, \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.1 \pm 1.0) \times 10^{-12}$	295	Takacs and Glass, 1973[1]	DF-EPR (a)
$(1.19 \pm 0.14) \times 10^{-11}$	249–416	Ravishankara, Wine, and Langford, 1979[2]	PLP-RF
$(6.01 \pm 0.32) \times 10^{-12}$	300	Husain, Plane, and Slater, 1981[3]	FP-RF
$(9.2 \pm 0.7) \times 10^{-12}$	~298	Jourdain, Le Bras, and Combourieu, 1981[4]	DF-EPR
$(1.12 \pm 0.045) \times 10^{-11}$	298±4	Cannon et al.,1984[5]	FP-LIF
$(1.1 \pm 0.1) \times 10^{-11}$	298	Ravishankara, Wine, and Wells, 1985[6]	PLP-RF
$(2.97 \pm 0.46) \times 10^{-11}$	170	Sims et al.,1994[7]	PLP-LIF (b,c)
$(1.16 \pm 0.04) \times 10^{-11}$	295		
$(8 \pm 1) \times 10^{-12}$	173	Atkinson, Jaramillo, and Smith, 1997[8]	FP-LIF (b,d)
$(1.5 \pm 0.4) \times 10^{-11}$	194		
$(1.0 \pm 0.3) \times 10^{-11}$	194		
$(1.3 \pm 0.2) \times 10^{-11}$	222		
$(1.1 \pm 0.1) \times 10^{-11}$	242		

Comments

(a) Rate coefficient obtained from a computer simulation of four reactions.

(b) Expansion of gas through a Laval nozzle to provide a collimated flow of cold gas at a uniform temperature, density and velocity.

(c) Experiments were carried out over the temperature range 23–295 K, with the measured rate coefficient decreasing with increasing temperature from $(1.07 \pm 0.04) \times 10^{-10} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 23 K to $(1.16 \pm 0.04) \times 10^{-11} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 295 K. Combined with the rate coefficients of Ravishankara et al.,[2] the temperature-dependent expression $k = (1.26 \pm 0.24) \times 10^{-11} (T/298)^{-(0.86 \pm 0.10)} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ was derived.

(d) Rate coefficients were measured over the temperature range 76–242 K, with the rate coefficient decreasing from $(3.0 \pm 0.5) \times 10^{-11} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 92 K and $(2.9 \pm 0.9) \times 10^{-11} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 76 K to $(1.1 \pm 0.1) \times 10^{-11} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 242 K. Above 150 K the rate coefficient was independent of temperature, within the experimental uncertainties.

Preferred Values

$k = 1.1 \times 10^{-11} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$, independent of temperature over the range 200–420 K.

Reliability

$\Delta \log k = \pm 0.10$ over the temperature range 200–420 K.

Comments on Preferred Values

The two studies of Sims et al.[7] and Atkinson et al.,[8] carried out using expansions through a Laval nozzle to achieve temperatures down to 23 K[7] and 76 K,[8] both show reaction rate coefficients which increase with decreasing temperature. However, while Sims et al.[7] observed that the rate coefficient at 170 K is markedly higher (by a factor of ~2.5) than the room temperature rate coefficient, Atkinson et al.[8] find the rate coefficient to be independent of temperature down to ~150–170 K. The data of Atkinson et al.[8] are therefore consistent with the earlier study of Ravishankara et al.[2] which also showed a temperature-independent rate coefficient over the range 249–416 K.

The preferred 298 K rate coefficient is an average of the room temperature rate coefficients of Ravishankara et al.,[2,6] Jourdain et al.,[4] Cannon et al.,[5] and Sims et al.[7] Based on the results of the temperature-dependent studies of Ravishankara et al.[2] and Atkinson et al.,[8] a temperature-independent rate coefficient is assumed over the range 200–420 K.

References

[1] G. A. Takacs and G. P. Glass, J. Phys. Chem. **77**, 1060 (1973).

[2] A. R. Ravishankara, P. H. Wine, and A. O. Langford, Chem. Phys. Lett. **63**, 479 (1979).

[3] D. Husain, J. M. C. Plane, and N. K. H. Slater, J. Chem. Soc. Faraday Trans. 2 **77**, 1949 (1981).

[4] J. L. Jourdain, G. Le Bras, and J. Combourieu, Chem. Phys. Lett. **78**, 483 (1981).

[5] B. D. Cannon, J. S. Robertshaw, I. W. M. Smith, and M. D. Williams, Chem. Phys. Lett. **105**, 380 (1984).

[6] A. R. Ravishankara, P. H. Wine, and J. R. Wells, J. Chem. Phys. **83**, 447 (1985).

[7] I. R. Sims, I. W. M. Smith, D. C. Clary, P. Bocherel, and B. R. Rowe, J. Chem. Phys. **101**, 1748 (1994).

[8] D. B. Atkinson, V. I. Jaramillo, and M. A. Smith, J. Phys. Chem. A **101**, 3356 (1997).
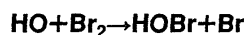
$HO+Br_2 \rightarrow HOBr+Br$

$\Delta H° \geq -14 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.2\pm0.7)\times10^{-11}$	298±2	Poulet, Laverdet, and Le Bras, 1983[1]	DF-LIF/EPR
$(5.28\pm0.63)\times10^{-11}$	298±3	Loewenstein and Anderson, 1984[2]	DF-RF
$(2.8\pm1.2)\times10^{-11}$	262–303	Boodaghians, Hall, and Wayne, 1987[3]	DF-RF (a)
$(3.4\pm1.2)\times10^{-11}$	293±2		
$1.98\times10^{-11}\exp[(238\pm70)/T]$	235–357	Gilles, Burkholder, and Ravishankara, 1999[4]	PLP-LIF
$(4.80\pm0.70)\times10^{-11}$	298		
$1.8\times10^{-11}\exp[(235\pm50)/T]$	230–360	Bedjanian, Le Bras, and Poulet, 1999[5]	DF-MS
3.96×10^{-11}	298		

Comments

(a) A least-squares fit of the measured rate coefficients results in $k=5.8\times10^{-10}\exp[-(866\pm1107)/T]$ cm^3 molecule^{-1} s^{-1}, consistent with a temperature-independent rate coefficient over the small temperature range studied.

Preferred Values

$k=4.3\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=1.9\times10^{-11}\exp(240/T)$ cm^3 molecule^{-1} s^{-1}, over the temperature range 230–360 K.

Reliability
$\Delta \log k = \pm0.10$ at 298 K.
$\Delta(E/R) = \pm150$ K.

Comments on Preferred Values

The rate coefficient is reasonably well determined at room temperature, and the recommended value is the mean of those reported by Poulet et al.,[1] Loewenstein and Anderson,[2]

Boodaghians et al.,[3] Gilles et al.,[4] and Bedjanian et al.[5] Boodaghians et al.[3] found a near zero temperature dependence over the range 262–303 K, while Gilles et al.[4] and Bedjanian et al.[5] measured a small negative temperature dependence over the significantly wider temperature range of 230–360 K. Accordingly, the temperature dependence of Gilles et al.[4] and Bedjanian et al.[5] is preferred, and the pre-exponential factor A is adjusted to fit the preferred 298 K rate coefficient. Poulet et al.[1] Loewenstein and Anderson,[2] and Bedjanian et al.[5] determined that the products are Br+HOBr, with the alternative reaction pathway leading to HBr+BrO accounting for <1% of the overall reaction at 298 K.[2]

References

[1] G. Poulet, G. Laverdet, and G. Le Bras, Chem. Phys. Lett. **94**, 129 (1983).
[2] L. M. Loewenstein and J. G. Anderson, J. Phys. Chem. **88**, 6277 (1984).
[3] R. B. Boodaghians, I. W. Hall, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **83**, 529 (1987).
[4] M. K. Gilles, J. B. Burkholder, and A. R. Ravishankara, Int. J. Chem. Kinet. **31**, 417 (1999).
[5] Y. Bedjanian, G. Le Bras, and G. Poulet, Int. J. Chem. Kinet. **31**, 698 (1999).
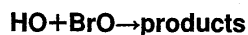
$HO+BrO \rightarrow products$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(7.5\pm4.2)\times10^{-11}$	300	Bogan et al., 1996[1]	DF-MS (a)

Comments

(a) BrO radicals were generated by passing a O_2–Br$_2$–He mixture through a microwave discharge. HO radicals were generated by the reaction of F atoms (generated in

a second microwave discharge) with H_2O. BrO radical concentrations were obtained by titration with NO and measurement of the resulting NO_2 by MS. HO radical concentrations were obtained by titration with Br$_2$ and

measurement of the depletion of Br_2 by MS. The rate coefficient was derived from modeling using a chemical mechanism involving 18 reactions.

Preferred Values

$k = 7.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of Bogan *et al.*[1] The reaction is believed[1] to proceed via

$$HO + BrO \rightarrow [HOOBr]^* \begin{cases} \rightarrow Br + HO_2 & \text{(a)} \\ \rightarrow HBr + O_2 & \text{(b)} \end{cases}$$
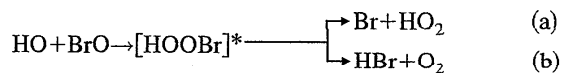
with channel (a) dominating.

References

[1] D. J. Bogan, R. P. Thorn, F. L. Nesbitt, and L. J. Stief, J. Phys. Chem. **100**, 14383 (1996).

$Br + NO_3 \rightarrow BrO + NO_2$
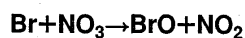
$\Delta H° = -32$ kJ $\cdot$ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.6 \pm 0.5) \times 10^{-11}$	298	Mellouki *et al.*, 1989[1]	DF-EPR (a)

Comments

(a) The decays of Br atoms in excess concentrations of the NO_3 radical were monitored by EPR. Computer simulations of the decays were carried out with a mechanism consisting of five reactions.

Preferred Values

$k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of Mellouki *et al.*[1]

References

[1] A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, J. Phys. Chem. **93**, 8017 (1989).

$BrO + NO_3 \rightarrow BrOO + NO_2$
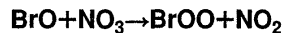
$\Delta H° = -53$ kJ $\cdot$ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(0.3 - 3.0) \times 10^{-12}$	298	Mellouki *et al.*, 1989[1]	DF-EPR (a)

Comments

(a) The decays of Br atoms and BrO radicals were monitored by EPR. Computer simulations of the results were carried out with a mechanism consisting of five reactions.

Preferred Values

$k = 1.0 \times 10^{-12} \, cm^3 \, molecule^{-1} \, s^{-1}$ at 298 K.

Reliability
$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The preferred value is based on the room temperature results of Mellouki *et al.*[1] This study,[1] using the discharge flow-EPR technique, is the only experimental study of this reaction to date. The preferred value is the geometric mean of the upper and lower limits,[1] which are encompassed within the stated uncertainty factor. The Br–O$_2$ bond is very weak and the bond energy has been estimated by Blake *et al.*[2] to be 4 kJ mol^{-1}. Thus the product BrOO will quickly decompose to yield Br+O$_2$.

References

[1] A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, J. Phys. Chem. **93**, 8017 (1989).
[2] J. A. Blake, R. J. Browne, and G. Burns, J. Chem. Phys. **53**, 3320 (1970).

$NO_3 + HBr \rightarrow HNO_3 + Br$
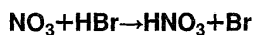
$\Delta H^\circ = -60.6 \, kJ \cdot mol^{-1}$

Rate coefficient data

$k/cm^3 \, molecule^{-1} \, s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\leq 1 \times 10^{-16}$	298	Mellouki *et al.*, 1989[1]	DF-EPR (a)
$(1.3 \pm 1.1) \times 10^{-16}$	298	Canosa-Mas *et al.*, 1989[2]	DF-A (b)

Comments

(a) The rate coefficient was derived from fitting the measured data to a complex mechanism.

(b) Discharge flow system with multipath absorption of NO$_3$. The rate coefficient was derived from fitting the measured data to a complex mechanism.

Preferred Values

$k < 1 \times 10^{-16} \, cm^3 \, molecule^{-1} \, s^{-1}$ at 298 K.

Comments on Preferred Values

The preferred value is the upper limit reported by Mellouki *et al.*[1] in a study using the discharge flow-EPR technique. Canosa-Mas *et al.*[2] reported a rate coefficient derived from fitting their data to a complex mechanism which, within the stated uncertainty limits, is consistent with the upper limit to the rate coefficient reported by Mellouki *et al.*[1]

References

[1] A. Mellouki, G. Poulet, G. Le Bras, R. Singer, J. P. Burrows, and G. K. Moortgat, J. Phys. Chem. **93**, 8017 (1989).
[2] C. E. Canosa-Mas, S. J. Smith, S. Toby, and R. P. Wayne, J. Chem. Soc. Faraday Trans. 2 **85**, 709 (1989).

$$BrO + HO_2 \rightarrow HOBr + O_2 \quad (1)$$

$$\rightarrow HBr + O_3 \quad (2)$$
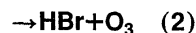
$\Delta H°(1) \geqslant -190 \, kJ \cdot mol^{-1}$

$\Delta H°(2) = -28 \, kJ \cdot mol^{-1}$

Rate coefficient data $(k = k_1 + k_2)$

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.4 \pm 1.0) \times 10^{-11}$	298	Bridier, Veyret, and Lesclaux, 1993[1]	FP-UVA (a)
$4.77 \times 10^{-12} \exp[(580 \pm 100)/T]$	233–344	Larichev *et al.*, 1995[2]	DF-MS (b)
$(3.4 \pm 0.6) \times 10^{-11}$	303		
$2.5 \times 10^{-12} \exp[(520 \pm 80)/T]$	210–298	Elrod *et al.*, 1996[3]	DF-MS (c)
$(1.4 \pm 0.3) \times 10^{-11}$	298		
$3.13 \times 10^{-12} \exp[(536 \pm 206)/T]$	233–348	Li, Friedl, and Sander, 1997[4]	DF-MS (d)
$(1.73 \pm 0.61) \times 10^{-11}$	298		
$(2.05 \pm 0.64) \times 10^{-11}$	298		
$(2.0 \pm 0.6) \times 10^{-11}$	298	Cronkhite *et al.*, 1998[5]	PLP-IR/UVA (e)

Comments

(a) Flash photolysis of $Br_2-O_3-Cl_2-CH_3OH-O_2-He$ mixtures. HO_2 and BrO radical concentrations were monitored by UV absorption spectroscopy under conditions where the HO_2 radical and BrO radical concentrations were of a similar magnitude.

(b) Discharge flow system. BrO radicals were generated by the $O + Br_2$ reaction, and their concentrations were monitored by MS in an excess of HO_2 radicals. A preliminary report of this study was noted in Poulet *et al.*[6]

(c) Turbulent flow system at 130 mbar total pressure. Reactant and product species were monitored by CIMS. BrO radicals were produced by the $O + Br_2$ reaction and HO_2 radicals by the $H + O_2 + M$ reaction. k was determined by monitoring the BrO radical concentrations in an excess of HO_2.

(d) BrO and HO_2 was monitored by MS. BrO radicals were produced by the $Br + O_3$ or $O + Br_2$ reactions and HO_2 radicals by the $F + H_2O_2$ or $Cl + CH_3OH$ reactions. Experiments were carried out under conditions of both $[BrO] \gg [HO_2]$ and $[HO_2] \gg [BrO]$. A similar temperature dependence of k was observed in each case, but values of k determined with excess BrO were systematically ~20–25% higher than those in excess HO_2. With $[HO_2] \gg [BrO]$, a rate coefficient of $k(298 \, K) = (1.73 \pm 0.61) \times 10^{-11} cm^3$ molecule^{-1} s^{-1} was obtained, and with $[BrO] \gg [HO_2]$, a rate coefficient of $k(298 \, K) = (2.05 \pm 0.64) \times 10^{-11} cm^3$ molecule^{-1} s^{-1} was obtained.

(e) Pulsed laser photolysis of $Cl_2-CH_3OH-O_2-Br_2-O_3-N_2$ mixtures. HO_2 and BrO radical concentrations were monitored simultaneously by infrared tunable diode laser absorption spectroscopy and UV absorption spectroscopy, respectively. Rate coefficients k were determined with $[HO_2] \gg [BrO]$.

Preferred Values

$k = 2.3 \times 10^{-11} cm^3$ molecule^{-1} s^{-1} at 298 K.

$k = 3.7 \times 10^{-12} \exp(545/T) cm^3$ molecule^{-1} s^{-1} over the temperature range 210–350 K.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

Disregarding the early study of Cox and Sheppard,[7] which gave a very low value for k, the remaining results at 298 K fall into two groups. There are two studies[1,2] which give values of k of $\sim 3 \times 10^{-11} cm^3$ molecule^{-1} s^{-1} and more recent measurements,[3-5] which give significantly lower values of k in the range $(1.4–2.1) \times 10^{-11} cm^3$ molecule^{-1} s^{-1}, despite very similar techniques having been used in some of the studies in the two groups. However, when the temperature dependence of k has been measured,[2-4] the values of E/R are in excellent agreement despite differences in the absolute values of k obtained. This points strongly to systematic errors in some of the studies.

The preferred value at 298 K is the mean of the rate coefficients of Bridier *et al.*,[1] Larichev *et al.*,[2] Elrod *et al.*,[3] Li *et al.*,[4] and Cronkhite *et al.*,[5] with substantial uncertainty limits. The preferred Arrhenius expression for k is obtained by taking the mean of the very similar values of E/R from the studies of Larichev *et al.*,[2] Elrod *et al.*,[3] and Li *et al.*[4] and combining it with a pre-exponential factor adjusted to give the preferred value of k at 298 K.

Several studies[2-4] have shown that the major product is HOBr. Larichev *et al.*[2] were unable to obtain evidence for O_3 formation in their mass spectrometric study of the reaction and set an upper limit for the branching ratio of k_2/k

<0.015. From a study of the reverse reaction at above room temperature, Mellouki et al.[8] have determined, by extrapolation, that the yield of HBr+O_3 is negligible (<0.01%) down to 200 K. Furthermore, k appears to be independent of pressure over the range covered by the studies to date of 1 mbar–1 bar,[1–5] and there is no evidence for stable adduct formation. Thus all of the available data suggests that channel (1) is the sole pathway over the temperature range of the preferred values.

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$$BrO+O_3 \rightarrow Br+2O_2 \quad (1)$$
$$\rightarrow OBrO+O_2 \quad (2)$$
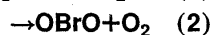
$\Delta H°(1) = -151 \text{ kJ·mol}^{-1}$
$\Delta H°(2) = 111 \text{ kJ·mol}^{-1}$

Rate coefficient data ($k=k_1+k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\sim10^{-17}$	318–343	Rattigan, Cox, and Jones, 1995[1]	P-AS (a)
$k_2=7\times10^{-14}\exp[-(3100\pm350)/T]$	318–343		
$k_2=2.1\times10^{-18}$	298*		
$<(2.1\pm0.7)\times10^{-17}$	298	Rowley et al., 1996[2]	FP-AS (b)
$k_2=(1.66\pm0.11)\times10^{-18}$	298		

Comments

(a) Photolysis of Br_2–O_3 mixtures at 380–480 nm in N_2 or O_2 bath gas at total pressures in the range 16–1000 mbar. Time-resolved UV absorption spectroscopy was used to monitor the concentrations of O_3, Br_2, and BrO radicals before, during, and after irradiation. OBrO was also detected in absorption in the wavelength range 400–600 nm.

(b) Flash photolysis-longpath UV absorption technique. BrO radicals were produced by photolysis at $\sim$400 nm of Br_2 in an excess of O_3. Time-resolved UV/visible absorption spectra of BrO were recorded over the range 234–367 nm and of OBrO over the range 425–558 nm. The BrO decay was largely due to the BrO+BrO reaction but deviations from second-order behavior were observed at high O_3 concentrations, and attributed to the BrO+O_3 reaction. The upper limit was derived from an analysis of the [BrO] temporal profiles at high O_3 concentrations.

Preferred Values

$k<2\times10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Comments on Preferred Values

The two most recent studies of Rattigan et al.[1] and Rowley et al.[2] are in good agreement and set a lower upper limit to the rate coefficient for this reaction than did previous studies.[3,4] The preferred upper limit to k at 298 K is therefore based on the results reported by Rattigan et al.[1] and Rowley et al.[2]

Previously, the reaction of BrO with O_3 had been assumed to occur exclusively by channel (1), but the positive identification of OBrO as a reaction product indicates that channel (2) is likely to be significant. The existing determinations of k_2 are in good agreement,[1,2] but involve significant uncertainties. Further studies are necessary before a branching ratio can be recommended.

References

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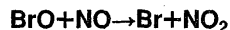
$BrO + NO \rightarrow Br + NO_2$

$\Delta H^\circ = -65 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.2 \pm 0.4) \times 10^{-11}$	298	Clyne and Watson, 1975[1]	DF-MS (a)
$7.11 \times 10^{-12} \exp[(296 \pm 10)/T]$	230–425	Leu, 1979[2]	DF-MS (a)
$(1.89 \pm 0.16) \times 10^{-11}$	298		
$1.28 \times 10^{-11} \exp[(181 \pm 46)/T]$	224–398	Watson, Sander, and Yung, 1979[3]	FP-UVA (b)
$(2.15 \pm 0.25) \times 10^{-11}$	298		
$(2.15 \pm 0.18) \times 10^{-11}$	298	Ray and Watson, 1981[4]	DF-MS (a)

Comments

(a)   BrO radicals were produced by the $O + Br_2$ reaction and monitored by MS in an excess of NO.

(b)   BrO radicals were produced by the flash photolysis of $Br_2 - O_2$ mixtures in the presence of an excess of NO. BrO radical concentrations were monitored by UV absorption at 339 nm. k was observed to be independent of pressure over the range 130–930 mbar of He or N_2.

Preferred Values

$k = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ at 298 K.

$k = 8.7 \times 10^{-12} \exp(260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ over the temperature range 220–430 K.
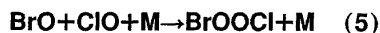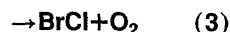
Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta (E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

The results of the three low pressure mass spectrometric studies of Clyne and Watson,[1] Leu,[2] and Ray and Watson[4]

and the high pressure UV absorption study of Watson *et al.*,[3] all of which used pseudofirst order conditions, are in excellent agreement at 298 K and are considered to be more reliable than the earlier low pressure UV absorption study of Clyne and Cruse.[5] The results of the two temperature dependence studies[2,3] are in good agreement. The preferred Arrhenius expression is derived from a least-squares fit to all the data of Clyne and Watson,[1] Leu,[2] Watson *et al.*,[3] and Ray and Watson.[4] By combining the data reported in the high pressure UV absorption study[3] with those from the mass spectrometric studies,[1,2,4] this reaction does not exhibit any observable pressure dependence between 1 mbar and 1 bar total pressure. The temperature dependencies of the rate coefficients for the analogous ClO and HO_2 reactions are also negative and similar in magnitude.

References

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$BrO + NO_2 + M \rightarrow BrONO_2 + M$

$\Delta H^\circ = -106 \text{ kJ} \cdot \text{mol}^{-1}$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(5.0 \pm 1.0) \times 10^{-31} [N_2]$	298	Sander, Ray, and Watson, 1981[1]	DF-MS/FP-UVA (a)
$(4.2 \pm 0.8) \times 10^{-31} (T/300)^{-2.0} [O_2]$	263–343	Danis *et al.*, 1990[2]	PLP-MS (b)
$5.4 \times 10^{-31} (T/298)^{-3.2} [N_2]$	248–346	Thorn, Daykin, and Wine, 1993[3]	PLP-UVA (c)

Comments

(a) In the DF-MS study the pressure range was 1.3–8 mbar, while the total pressure in the FP-UVA study ranged from 57–933 mbar. In the DF-MS study, BrO radicals were produced by the reaction $Br+O_3 \rightarrow BrO+O_2$, and in the FP-UVA study BrO radicals were formed by the reaction of $O(^3P)$ atoms (from the photolysis of O_2) with Br_2. A major portion of the falloff curve was observed and analyzed with a fitted value of $F_c=0.4$ at 298 K.

(b) BrO radicals were produced by the photolysis of O_3 at 248 nm in the presence of Br_2. Rate coefficients were measured at total pressures below 16 mbar. Falloff curves were extrapolated using $F_c=\exp(-T/325)$.

(c) BrO radicals were generated by the photolysis of Br_2–NO_2–N_2 mixtures at 351 nm, and were monitored by long-path (550 cm) absorption at 338.3 nm. The total pressure was varied over the range 21–1060 mbar. The data were analyzed with F_c $=\exp(-T/327)$, based on the fitted value of $F_c=0.4$ of Sander et al.[1] and the temperature dependence of F_c preferred in the present evaluation (see Introduction). If a value of $F_c=0.6$ is used, a rate coefficient of k_0 $=5.2\times10^{-31}(T/300)^{-3.2}[N_2]$ cm^3 $molecule^{-1}$ s^{-1} is obtained.

Preferred Values

$k_0=4.7\times10^{-31}(T/300)^{-3.1}[N_2]$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 240–350 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = +1$.

Comments on Preferred Values

The preferred values are based on the data of Sander et al.,[1] Danis et al.,[2] and Thorn et al.[3] The reverse dissociation reaction $BrONO_2+M \rightarrow BrO+NO_2+M$ has recently been investigated by Orlando and Tyndall[4] over the temperature range 320–340 K and at total pressures between 133 and 1330 mbar. The rate coefficient data[4] were combined with *recommended values for the recombination reaction*[5,6] to derive from a second- and third-law analysis the reaction enthalpy of (118.0 ± 6) kJ mol^{-1} for the dissociation reacti⌐

High-pressure rate coefficients

Rate coefficient data

k_∞ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.0^{+0.5}_{-1.0})\times10^{-11}$	298	Sander, Ray, and Watson, 1981[1]	DF-MS/FP-UVA (a)
$1.4\times10^{-11}(T/300)^{-1.2}$	248–346	Thorn, Daykin, and Wine, 1993[3]	PLP-UVA (b)

Comments

(a) See comment (a) for k_0. Extrapolation of falloff curve with a fitted value of $F_c=0.4$.

(b) See comment (c) for k_0. If instead of F_c $=\exp(-T/327)$, a fixed value of $F_c=0.6$ is employed in fitting the falloff curves, a rate coefficient of $k_\infty=6.9\times10^{-12}(T/300)^{-2.9}$ cm^3 $molecule^{-1}$ s^{-1} is obtained.

Preferred Values

$k_\infty=1.4\times10^{-11}(T/300)^{-1.2}$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 240–350 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on the data of Thorn et al.[3] which are in good agreement with the data of Sander et al.[1] at 298 K.

References

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$$\text{BrO}+\text{ClO}\rightarrow\text{Br}+\text{OClO} \quad (1)$$

$$\rightarrow\text{Br}+\text{ClOO} \quad (2)$$

$$\rightarrow\text{BrCl}+\text{O}_2 \quad (3)$$

$$\rightarrow\text{Cl}+\text{OBrO} \quad (4)$$

$$\text{BrO}+\text{ClO}+\text{M}\rightarrow\text{BrOOCl}+\text{M} \quad (5)$$

$\Delta H^\circ(1) = -14\,\text{kJ}\cdot\text{mol}^{-1}$
$\Delta H^\circ(2) = -12\,\text{kJ}\cdot\text{mol}^{-1}$
$\Delta H^\circ(3) = -207\,\text{kJ}\cdot\text{mol}^{-1}$
$\Delta H^\circ(4) = 52\,\text{kJ}\cdot\text{mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

$k/\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$6.1\times10^{-12}\exp[(240\pm60)/T]$	220–400	Sander and Friedl, 1988[1]	FP-UVA (a)
$(1.29\pm0.18)\times10^{-11}$	298		
$4.7\times10^{-12}\exp[(320\pm60)/T]$	220–400	Friedl and Sander, 1988[2]	DF-MS (b)
$(1.29\pm0.19)\times10^{-11}$	298		
$2.59\times10^{-12}\exp[(445\pm84)/T]$	234–406	Turnipseed, Birks, and Calvert, 1991[3]	DF-MS (c)
$(1.08\pm0.20)\times10^{-11}$	304		
$k_1 = 6.7\times10^{-13}\exp[(622\pm94)/T]$	234–406		
$k_2 = 2.1\times10^{-12}\exp[(258\pm56)/T]$	234–406		
$k_3 = 1.9\times10^{-13}\exp[(513\pm86)/T]$	234–406		
Branching Ratios			
$k_1/k = 0.68\pm0.10$	220	Sander and Friedl, 1988[1]	(a)
$k_1/k = 0.59\pm0.10$	298		
$k_1/k = 0.55\pm0.07$	220	Friedl and Sander, 1988[2]	(b)
$k_1/k = 0.48\pm0.07$	298		
$k_1/k = 0.44\pm0.07$	400		
$k_2/k = 0.39\pm0.10$	220	Friedl and Sander, 1988[2]	(b)
$k_2/k = 0.40\pm0.10$	298		
$k_2/k = 0.44\pm0.10$	400		
$k_3/k = 0.06\pm0.03$	220	Friedl and Sander, 1988[2]	(b)
$k_3/k = 0.08\pm0.03$	298		
$k_3/k = 0.08\pm0.03$	400		
$k_1/k = 0.51\pm0.09$	250	Turnipseed, Birks, and Calvert, 1991[3]	(c)
$k_1/k = 0.48\pm0.07$	304		
$k_1/k = 0.39\pm0.07$	406		
$(k_2+k_3)/k = 0.46\pm0.07$	250	Turnipseed, Birks, and Calvert, 1991[3]	(c)
$(k_2+k_3)/k = 0.55\pm0.09$	304		
$(k_2+k_3)/k = 0.61\pm0.11$	406		
$k_3/k = 0.10\pm0.02$	250	Turnipseed, Birks, and Calvert, 1991[3]	(c)
$k_3/k = 0.09\pm0.02$	304		
$k_3/k = 0.09\pm0.02$	406		
$k_1/k = 0.53\pm0.05$	295	Bloss, 1999[4]	(d)
$k_4/k < 0.02$	295		

Comments

(a)　BrO, ClO, and OClO were detected using the temperature-dependent absorption cross sections measured in the same study. BrO radical decays were monitored with [ClO]>[BrO]. Measurement of the rate coefficient ratio k_1/k was based on $\Delta[\text{OClO}]/\Delta[\text{BrO}]$ as a function of time.

(b)　BrO, ClO, OClO, and BrCl were detected. BrO radical decays were measured in excess ClO. The branching ratios were based on the yields of OClO, Cl (after conversion to BrCl) and BrCl compared to the amounts of BrO and ClO reacted.

(c)　Dischage flow system with MS detection of BrO, ClO, OClO, and BrCl. BrO radical decays were monitored in the presence of a 10–60-fold excess of ClO radicals.

Branching ratios were based on the yields of OClO, ClO, and BrCl in the presence of the Cl atom scavengers HBr and C_2H_3Br.

(d) Flash photolysis system with UV absorption detection (using a coupled charge detector) of BrO, ClO, OClO, and OBrO using differential absorption spectroscopy. The branching ratio k_4/k was based on the absence of characteristic OBrO absorption in the region 400–500 nm during the BrO and ClO decays.

Preferred Values

$k_1 = 6.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2 = 6.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_3 = 1.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_1 = 1.6 \times 10^{-12} \exp(430/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.

$k_2 = 2.9 \times 10^{-12} \exp(220/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.

$k_3 = 5.8 \times 10^{-13} \exp(170/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220–400 K.

Reliability
$\Delta \log k_1 = \Delta \log k_2 = \Delta \log k_3 = \pm 0.1$ at 298 K.
$\Delta(E_1/R) = \Delta(E_2/R) = \Delta(E_3/R) = \pm 200$ K.

Comments on Preferred Values

The data base for this reaction is now extensive. Friedl and Sander,[2] using a discharge flow-mass spectrometry system, measured the overall rate coefficient over the temperature range 220–400 K and also over this temperature range determined directly the branching ratios for the reaction channels producing BrCl and OClO. In a separate study[1] the same authors, using flash photolysis–ultraviolet absorption techniques, measured the overall rate coefficient over the temperature range 220–400 K and pressure range 67–1000 mbar, and also determined the branching ratio for OClO production at 220 and 298 K. The results by these two independent techniques[1,2] are in excellent agreement, with the overall rate coefficient showing a negative temperature dependence. The study of Turnipseed et al.[3] also resulted in a comprehensive set of rate coefficient and branching ratio data. The overall rate coefficients from these three studies[1–3] are in good agreement at room temperature (within 20%) and are in excellent agreement at stratospheric temperatures.

Toohey and Anderson,[5] using discharge flow-resonance fluorescence/LMR techniques, reported room temperature values of the overall rate coefficient and the branching ratio for OClO production. They also found evidence for the direct production of BrCl in a vibrationally excited π state.[5] Poulet et al.,[6] using discharge flow-mass spectrometry techniques, reported room temperature values of the overall rate coefficient and branching ratios for OClO and BrCl production. Clyne and Watson[7] also studied this reaction using a discharge flow-MS system.

The results of the studies of Toohey and Anderson,[5] Sander and Friedl,[1] Friedl and Sander,[2] Poulet et al.,[6] Turnipseed et al.,[3] and Bloss[4] are in reasonably good agreement. The rate coefficients of Hills et al.,[8] using a discharge flow-mass spectrometry technique, were independent of temperature over the range 241–308 K and the room temperature rate coefficient was substantially lower than the average value from the above-mentioned studies.[1–3,5,6] Hills et al.[8] also reported no BrCl formation. In the flash photolysis study of Basco and Dogra[9] a different interpretation of the reaction mechanism was used; the reported rate coefficients were low and are not used in the evaluation of the rate coefficient for this reaction.

The recommended Arrhenius expressions for the individual reaction channels are taken from the studies of Friedl and Sander[2] and Turnipseed et al.,[3] which contain the most comprehensive sets of rate coefficient and branching ratio data. Both of these studies,[2,3] as well as that of Sander and Friedl,[1] show that OClO production by channel (1) becomes dominant at very low temperature. Both studies show an ~8% yield of BrCl by channel (3). The recommended expressions are consistent with the body of data from all studies except those of Refs. 8 and 9.

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$$BrO+BrO \rightarrow 2Br+O_2 \quad (1)$$

$$\rightarrow Br_2+O_2 \quad (2)$$

$$\rightarrow Br+OBrO \quad (3)$$

$$BrO+BrO+M \rightarrow Br_2O_2+M \quad (4)$$
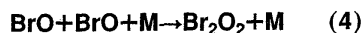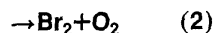
$\Delta H^\circ(1) = -16 \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta H^\circ(2) = -209 \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta H^\circ(3) = 24 \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta H^\circ(4) = -59 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data ($k=k_1+k_2+k_3+k_4$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.17\pm0.67)\times10^{-12}$	298	Clyne and Watson, 1975[1]	DF-MS
$9.58\times10^{-13} \exp[(255\pm195)/T]$	223–388	Sander and Watson, 1981[2]	(a)
$(2.17\pm0.68)\times10^{-12}$	298		
$(3.2\pm0.5)\times10^{-12}$	298	Lancar *et al.*, 1991[3]	(b)
$k_2=(4.7\pm1.5)\times10^{-13}$	298		
$(2.75\pm0.57)\times10^{-12}$	298	Mauldin, Wahner, and Ravishankara, 1993[4]	(c)
$k_2=(4.45\pm0.82)\times10^{-13}$	298		
$k_1=(2.49\pm0.42)\times10^{-12}$	298	Rowley *et al.*, 1996[5]	(d)
$k_2=(4.69\pm0.68)\times10^{-13}$	298		
$(2.8\pm0.5)\times10^{-12}$	298	Laszlo *et al.*, 1997[6]	(e)
$1.70\times10^{-12} \exp[(215\pm50)/T]$	204–388	Gilles *et al.*, 1997[7]	(f)
$(3.51\pm0.35)\times10^{-12}$	298		
$k_1=5.31\times10^{-12} \exp[-(211\pm59)/T]$	250–298	Harwood *et al.*, 1998[8]	(g)
$k_2=1.13\times10^{-14} \exp[(983\pm111)/T]$	250–298		
$k_4=(8.2\pm1.1)\times10^{-32}[\text{M}]$	222		
Branching Ratios			
$k_1/k=0.84\pm0.03$	298	Sander and Watson, 1981[1]	(a)
$k_1/k=0.84\pm0.01$	298	Mauldin, Wahner, and Ravishankara, 1993[4]	(c)
$k_1/k=0.68\pm0.05$	220		
$k_1/k=0.85\pm0.02$	298	Rowley *et al.*, 1996[5]	(d)

Comments

(a) Flash photolysis study with absorption spectroscopic detection of BrO radicals using the 7-0 band of the A–X system at 339 nm, for which a cross section of $(1.14\pm0.14)\times10^{-17} \text{cm}^2 \text{molecule}^{-1}$ was measured. The total pressure was 65–789 mbar of N_2. The branching ratio was determined from measurements with and without excess O_3 present, using two methods that gave the same result.

(b) Discharge flow-mass spectrometry study, in which rate coefficients were determined from measurements with and without excess O_3 present. The rate coefficient k_2 was obtained from BrO radical decays and Br_2 formation.

(c) Flash photolysis-longpath absorption technique. Measurements were made at 298 and 220 K over a pressure range of 100–800 mbar of He, N_2, and SF_6. The overall rate coefficient was found to be independent of pressure at 298 K, but at 220 K to increase from 2.0 $\times10^{-12} \text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ at 133 mbar to 3.1

$\times10^{-12} \text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ at 530 mbar. The branching ratio was found to be independent of pressure at 298 K and 220 K. An additional transient absorption feature was observed at 220 K and was tentatively attributed to Br_2O_2. BrO concentrations were determined using the absorption cross sections of Wahner *et al.*,[9] the cross section at 338.5 nm was 1.71 $\times10^{-17} \text{cm}^2 \text{molecule}^{-1}$ at 298 K and 2.21 $\times10^{-17} \text{cm}^2 \text{molecule}^{-1}$ at 220 K (0.2 nm *resolution*). The following expressions were recommended for atmospheric modeling: $k_1=4.0\times10^{-12} \exp(-190/T)$ $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$ and $k_2=4.2\times10^{-14} \exp(660/T)$ $\text{cm}^3 \text{molecule}^{-1}\text{s}^{-1}$.

(d) Flash photolysis-UV absorption technique, with detection of BrO radicals using time-resolved CCD detection in the A–X system at 400–470 nm. BrO radical concentrations were determined using the absorption cross sections of Wahner *et al.*[9] compensated for the change in resolution. Rate coefficients were obtained from measurements with and without excess O_3 present. OBrO was observed in the presence of high

concentrations of O_3, apparently due to the $BrO+O_3$ reaction and not to channel (3). The total pressure was 1000 mbar.

(e) Pulsed laser photolysis of $N_2O-Br_2-N_2$ mixtures, with absorption spectroscopic detection of BrO radicals. An absorption cross section of $(1.41\pm0.15)\times10^{-17}$ cm^2 molecule^{-1} at 338.5 nm was measured.

(f) Pulsed laser photolysis of $N_2O-Br_2-N_2$ mixtures, with absorption spectroscopic detection of BrO radicals. An absorption cross section of 1.63×10^{-17} cm^2 molecule^{-1} at 338.5 nm (0.5 nm resolution) was measured at 298 K. A similar temperature dependence of the absorption crosssection as observed by Wahner et al.[9] was obtained.

(g) Flash photolysis-absorption spectroscopy technique with detection of BrO radicals using time-resolved CCD detection in the A–X system at 400–470 nm. BrO concentrations were determined using the absorption cross sections of Wahner et al.[9] compensated for change in resolution and for temperature dependence. Rate coefficients were obtained from measurements with and without excess O_3 present. The total pressure was in the range 130–1000 mbar. In the presence of O_3 and below 250 K, departure from second-order kinetics for BrO was observed and a transient absorption attributed to Br_2O_2 was observed. The overall rate coefficient was pressure dependent in this temperature regime and the results were analyzed to yield a value for the rate coefficient for dimer formation [channel (4)] at 222 K. The formation of the dimer apparently replaced the bimolecular channels at low temperature, and the expressions for k_1 and k_2 only apply to temperatures >250 K.

Preferred Values

$k_1=2.7\times10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 250–390 K.
$k_2=4.8\times10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k=3.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k_2=2.9\times10^{-14}$ exp$(840/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250–390 K.
$k=1.6\times10^{-12}$ exp$(210/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200–390 K.

Reliability

$\Delta \log k_1=\Delta \log k_2=\pm0.1$ at 298 K.
$\Delta(E_1/R)=\Delta(E_2/R)=\pm200$ K.

Comments on Preferred Values

The total rate coefficient for the $BrO+BrO$ reaction has been studied by a variety of techniques, including discharge flow-mass spectrometry and flash photolysis–ultraviolet absorption spectroscopy. The results from the latter technique depend on the value used for the absorption cross section of BrO at the monitoring wavelength, usually 338.5 nm (the

(7-0) band of the A–X transition). The absorption cross section of BrO was remeasured by Gilles et al.[7] with the values obtained being given by the expression $\sigma(BrO)=[3.29-(5.58\times10^{-3})T]\times10^{-17}$ cm^2 molecule^{-1} at 338.5 nm. At a comparable resolution this expression gives values of $\sigma(BrO)\sim10\%$ larger than those of Wahner et al.[9] and employed by most of the earlier studies. When this difference is taken into account, the 298 K rate coefficients from the flash photolysis–absorption spectroscopy studies are in excellent agreement with the discharge flow studies (to within 10%), except for the study of Turnipseed et al.[10] The mean 298 K rate coefficient is 3.2×10^{-12} cm^3 molecule^{-1} s^{-1} independent of pressure.

The branching ratio between the bimolecular channels has been measured directly in the studies cited,[1,4,5] and by Turnipseed et al.[10] and indirectly by Jaffe and Mainquist[11] from 258–333 K, Cox et al.[12] from 278–348 K, and by Rattigan et al.[13] at 298 K. All studies are in agreement that $k_1/k=0.85\pm0.03$ at 298 K and that the termolecular channel increases in importance with decreasing temperature.

The temperature dependence is complicated by a pressure dependence of the rate coefficients at low temperatures (<250 K), as observed by Mauldin et al.[4] and Harwood et al.[8] The rate coefficients at <250 K increase with pressure, which Harwood et al.[8] associated with the formation of an unstable Br_2O_2 dimer, which was observed spectroscopically by both Mauldin et al.[4] and Harwood et al.[8] The study of Gilles et al.,[7] which covers the largest temperature range and was conducted at low total pressures, shows a small negative temperature dependence for the overall rate coefficient. The preferred values are based on the above 298 K rate coefficient of $k=3.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1} and an $(E/R)=-210$ K, resulting in $k=1.6\times10^{-12}$ exp$(210/T)$ cm^3 molecule^{-1} s^{-1}. The recommended channel-specific rate coefficients are based on the values of $k_1/k=0.85$ at 298 K and $k_1/k=0.68$ at 220 K.

References

[1] M. A. A. Clyne and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 **71**, 336 (1975).

[2] S. P. Sander and R. T. Watson, J. Phys. Chem. **85**, 4000 (1981).

[3] I. T. Lancar, G. Laverdet, G. Le Bras, and G. Poulet, Int. J. Chem. Kinet. **23**, 37 (1991).

[4] R. L. Mauldin III, A. Wahner, and A. R. Ravishankara, J. Phys. Chem. **97**, 7585 (1993).

[5] D. M. Rowley, M. H. Harwood, R. A. Freshwater, and R. L. Jones, J. Phys. Chem. **100**, 3020 (1996).

[6] B. Laszlo, R. E. Huie, M. J. Kurylo, and A. W. Miziolek, J. Geophys. Res. **102**, 1523 (1997).

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[8] M. H. Harwood, D. M. Rowley, R. A. Cox, and R. L. Jones, J. Phys. Chem. A **102**, 1790 (1998).

[9] A. Wahner, A. R. Ravishankara, S. P. Sander, and R. R. Friedl, Chem. Phys. Lett. **152**, 507 (1988).

[10] A. A. Turnipseed, J. W. Birks, and J. G. Calvert, J. Phys. Chem. **94**, 7477 (1990).

[11] S. Jaffe and W. K. Mainquist, J. Phys. Chem. **84**, 3277 (1980).

[12] R. A. Cox, D. W. Sheppard, and M. P. Stevens, J. Photochem. **19**, 189 (1982).

[13] O. V. Rattigan, R. A. Cox, and R. L. Jones, J. Chem. Soc. Faraday Trans. **91**, 4189 (1995).

4.4. Iodine Species

$O + I_2 \rightarrow IO + I$
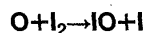
$\Delta H^\circ = -89 \, \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.38 \pm 0.44) \times 10^{-10}$	298	Ray and Watson, 1981[1]	DF-MS (a)
$(1.4 \pm 0.4) \times 10^{-10}$	298	Laszlo, Kurylo, and Huie, 1995[2]	PLP-AS (b)
$(1.3 \pm 0.15) \times 10^{-10}$	295	Hölscher, Fockenberg, and Zellner, 1998[3]	PLP-LIF (c)

Comments

(a)   MS detection of I_2 in a large excess of $O(^3P)$ atoms. The $O(^3P)$ atom concentrations were determined by titration with NO_2. The total pressure was ~ 2.6 mbar.

(b) $O(^3P)$ atoms were produced by pulsed laser photolysis of N_2O at 193 nm in the presence of I_2, at total pressures of ~ 260 mbar of N_2. The I_2 concentrations used were comparable to those of $O(^3P)$ atoms. The I_2 and IO radical concentrations were monitored simultaneously by absorption spectroscopy at 530 nm and at 340–435 nm, respectively, and values of k were derived by modeling the I_2 and IO radical time–concentration profiles.

(c) $O(^3P)$ atoms were produced by pulsed laser photolysis of N_2O at 193 nm in the presence of an excess of I_2, at total pressures of 40 mbar of N_2. IO radical concentrations were monitored by LIF at 445.05 nm.

Preferred Values

$k = 1.4 \times 10^{-10} \, \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The recommended rate coefficient is based on the data of Ray and Watson,[1] Laszlo *et al.*,[2] and Hölscher *et al.*,[3] obtained using totally different experimental techniques and which are in excellent agreement. The rate coefficient is large, approaching the gas kinetic collisional value and suggesting a near zero temperature dependence for k. This is in accord with the molecular beam study of the reaction by Parrish and Herschbach.[4]

References

[1] G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 2955 (1981).

[2] B. Laszlo, M. J. Kurylo, and R. E. Huie, J. Phys. Chem. **99**, 11701 (1995).

[3] D. Hölscher, Chr. Fockenberg, and R. Zellner, Ber. Bunsenges. Phys. Chem. **102**, 716 (1998).

[4] D. D. Parrish and D. R. Herschbach, J. Am. Chem. Soc. **95**, 6133 (1973).

$O + IO \rightarrow O_2 + I$
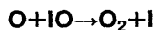
$\Delta H^\circ = -258 \, \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.2 \pm 0.5) \times 10^{-10}$	298	Laszlo, Kurylo, and Huie, 1995[1]	PLP-AS (a)
$(1.5 \pm 0.7) \times 10^{-10}$	298	Payne *et al.*, 1998[2]	DF-MS (b)

Comments

(a) O(^{3}P) atoms were produced by pulsed laser photolysis of N_2O at 193 nm in the presence of I_2, at total pressures of ~260 mbar of N_2. The I_2 concentrations used were comparable to those of O(^{3}P) atoms. The I_2 and IO radical concentrations were monitored simultaneously by absorption spectroscopy at 530 nm and at 340–435 nm, respectively, and values of k were derived by modeling the I_2 and IO radical time–concentration profiles.

(b) IO radical concentrations were monitored by MS in the presence of a large excess of O(^{3}P) atoms. The total pressure was ~1.3 mbar of He.

Preferred Values

$k = 1.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

Prior to the two recent studies cited in the table,[1,2] only estimates of the rate coefficient for this reaction were available. The preferred value is the mean of the rate coefficients obtained by Laszlo et al.[1] and Payne et al.,[2] which are in good agreement and were obtained using quite different experimental techniques. The value of the rate coefficient is large, approaching the gas kinetic collisional value and suggesting a near zero temperature dependence of k.

References

[1] B. Laszlo, M. J. Kurylo, and R. E. Huie, J. Phys. Chem. **99**, 11701 (1995).
[2] W. A. Payne, R. P. Thorne, Jr., F. L. Nesbitt, and L. J. Stief, J. Phys. Chem. A **102**, 6247 (1998).

I+HO$_2$→HI+O$_2$
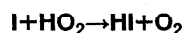
$\Delta H° = -94.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.47 \times 10^{-11} \exp[-(1090 \pm 130)/T]$	283–353	Jenkin et al., 1990[1]	(a)
$(3.8 \pm 1.0) \times 10^{-13}$	298		

Comments

(a) Two experimental methods were used. The first technique involved a discharge flow system with EPR detection of I atoms (directly) and of HO$_2$ radicals after conversion to HO radicals (by reaction with NO). The first-order decays of HO$_2$ radicals in excess I atoms were measured, resulting in a rate coefficient of $k = (3.1 \pm 1.2) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K. The second technique, which provided the temperature dependence, employed the molecular modulation method with UV absorption detection of HO$_2$ radicals, and with the I atom concentration being determined from the observed modulation of the I_2 absorption at 500 nm. Excess I atoms were employed, and the HO$_2$ radical self-reaction competed with the I+HO$_2$ reaction. The best analysis gave $k = (4.17 \pm 0.4) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K. The Arrhenius expression was obtained from the mean of the discharge flow and molecular modulation determinations at 298 K and the E/R obtained from a least-squares fit to the temperature-dependent data.

Preferred Values

$k = 3.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.5 \times 10^{-11} \exp(-1090/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 280–360 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

The preferred values are based on the two experimental studies reported by Jenkin et al.,[1] which are the only reported measurements for this reaction. The values of the rate coefficient at 298 K from the two studies agree quite well, although both studies exhibited significant experimental error. The Arrhenius expression suggested by Jenkin et al.[1] is accepted for the temperature dependence.

References

[1] M. E. Jenkin, R. A. Cox, A. Mellouki, G. Le Bras, and G. Poulet, J. Phys. Chem. **94**, 2927 (1990).

$I+O_3 \rightarrow IO+O_2$
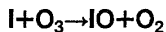
$\Delta H^\circ = -133 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.6\pm3.0)\times10^{-13}$	303	Jenkin and Cox, 1985[1]	MM-AS (a)
$(9.5\pm1.5)\times10^{-13}$	298	Sander, 1986[2]	FP-AS
$2.3\times10^{-11}\exp[-(886\pm15)/T]$	231–337	Buben *et al.*, 1990[3]	DF-RF
$(1.2\pm0.1)\times10^{-12}$	298		
$2.3\times10^{-11}\exp[-(860\pm100)/T]$	240–370	Turnipseed *et al.*, 1995[4]	PLP-LIF
$(1.38\pm0.08)\times10^{-12}$	298		
$1.6\times10^{-11}\exp[-(750\pm194)/T]$	243–295	Hölscher, Fockenberg, and Zellner, 1998[5]	PLP-LIF
$(1.2\pm0.1)\times10^{-12}$	295		

Comments

(a) Modulated photolysis of I_2–O_3 mixtures at 570 nm and a total pressure of 34 mbar. IO radicals were monitored in absorption at 426.9 nm.

Preferred Values

$k = 1.2\times10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.9\times10^{-11}\exp(-830/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–370 K.

Reliability

$\Delta \log k = \pm0.15$ at 298 K.

$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The studies cited above,[1-5] which used a variety of techniques, are in excellent agreement. The preferred value of k at 298 K is the mean of the values obtained by Jenkin and Cox,[1] Sander,[2] Buben *et al.*,[3] Turnipseed *et al.*,[4] and Hölscher *et al.*[5] The preferred Arrhenius expression for k is obtained by combining the mean of the values of E/R from the studies of Buben *et al.*,[3] Turnipseed *et al.*,[4] and Hölscher *et al.*[5] with a pre-exponential factor adjusted to give the preferred value of k at 298 K.

References

[1] M. E. Jenkin and R. A. Cox, J. Phys. Chem. **89**, 192 (1985).

[2] S. P. Sander, J. Phys. Chem. **90**, 2194 (1986).

[3] S. N. Buben, I. K. Larin, N. A. Messineva, and E. M. Trofimova, Khim. Fiz. **9**, 116 (1990).

[4] A. A. Turnipseed, M. K. Gilles, J. B. Burkholder, and A. R. Ravishankara, Chem. Phys. Lett. **242**, 427 (1995).

[5] D. Hölscher, Chr. Fockenberg, and R. Zellner, Ber. Bunsenges. Phys. Chem. **102**, 716 (1998).

$I+NO+M \rightarrow INO+M$

$\Delta H^\circ = -75.7 \text{ kJ} \cdot \text{mol}^{-1}$

Low-pressure rate coefficients

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.0\pm2.5)\times10^{-33}(T/300)^{-1.0}$ [He]	320–450	van den Bergh and Troe, 1976[1]	PLP-UVA (a)
$(1.6\pm0.5)\times10^{-32}$ [N_2]	330	van den Bergh, Benoit-Guyot, and Troe, 1977[2]	PLP-UVA (b)
$(9.5\pm3)\times10^{-33}$ [Ar]	330		
$(1.05\pm0.3)\times10^{-32}$ [Ar]	298		
$(1.03\pm0.06)\times10^{-32}(T/300)^{-1.1}$ [Ar]	298–328	Basco and Hunt, 1978[3]	FP (c)

Comments

(a) Photolysis of I_2 at 694 nm in the presence of NO and He. The He pressure was varied between 1 and 200 bar. I_2 and INO spectra were observed.

(b) As in comment (a). The effect of the different bath gases was studied. The rate coefficient for M=Ar at 298 K was calculated from the measured rate coefficient at 330 K and the temperature dependence reported by van den Bergh and Troe.[1]

(c) Photolysis of I_2 in the presence of NO and Ar.

Preferred Values

$k_0 = 1.8 \times 10^{-32} (T/300)^{-1.0}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 290–450 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred values are based on the rate coefficients for M=Ar determined by van den Bergh et al.[2] and Basco and Hunt,[3] which agree remarkably well. The collision efficiencies for He, Ar, and N_2 follow the usual trend. The transition to the high pressure limit is of no importance for pressures below 1 bar.

High-pressure rate coefficients

Rate coefficient data

k_∞ /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$\geqslant 1.7 \times 10^{-11}$	330	van den Bergh and Troe, 1976[1]	PLP-UVA (a)

Comments

(a) As for comment (a) for k_0. Based on a falloff extrapolation with $F_c = 0.6$.

Preferred Values

$k_\infty - 1.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ over the temperature range 300–400 K.

Comments on Preferred Values

The preferred values are based on the only measurement, of van den Bergh and Troe,[1] and a value of $F_c = 0.6$.

References

[1] H. van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).
[2] H. van den Bergh, N. Benoit-Guyot, and J. Troe, Int. J. Chem. Kinet. **9**, 223 (1977).
[3] N. Basco and J. E. Hunt, Int. J. Chem. Kinet. **10**, 733 (1978).

$I+NO_2+M \rightarrow INO_2+M$

$\Delta H° = -79.8 \text{ kJ} \cdot \text{mol}^{-1}$

Low-pressure rate coefficients

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.5 \times 10^{-31}(T/300)^{-1}$ [He]	320–450	van den Bergh and Troe, 1976[1]	PLP-UVA (a)
1.62×10^{-31} [He]	330	van den Bergh, Benoit-Guyot, and Troe, 1977[2]	PLP-UVA (b)
2.6×10^{-31} [N_2]	330		
$(9.5 \pm 3.5) \times 10^{-32}$ [He]	298	Mellouki *et al.*, 1989[3]	DF-EPR (c)
3.1×10^{-31} [N_2]	298	Buben *et al.*, 1990[4]	FP-RF (d)

Comments

(a) Derived from the NO_2 catalyzed recombination of I atoms, with I atoms being produced by photolysis of I_2 at 694 nm. The falloff curve was measured from 1 to 200 bar of He, and only a short extrapolation to k_0 was required.

(b) As in comment (a). The efficiency of 26 bath gases were studied.

(c) Measurements were performed over the total pressure range 0.8–2.9 mbar.

(d) I atoms were generated by the photolysis of CH_3I in a flow system with NO_2–N_2 mixtures. The bath gases N_2, O_2, Ar, and He were studied at total pressures between 0.7 and 13 mbar.

Preferred Values

$k_0 = 3.0 \times 10^{-31}(T/300)^{-1}$ [N_2] $\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ over the temperature range 290–450 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 298 K.

$\Delta n = \pm 1.$

Comments on Preferred Values

The preferred values are based on the results of the studies of van den Bergh and Troe,[1] van den Bergh *et al.*,[2] and Buben *et al.*[4] The data of Mellouki *et al.*[3] for M=He are also consistent with the data of van den Bergh and Troe,[1] van den Bergh *et al.*,[2] and Buben *et al.*[4] Falloff extrapolations are made with a fitted[1] value of $F_c = 0.63$ near 300 K.

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
6.6×10^{-11}	320–450	van den Bergh and Troe, 1976[1]	PLP-UVA (a)

Comments

(a) See comment (a) for k_0. Extrapolation of the falloff curve towards the high pressure limit uses a fitted value of $F_c = 0.63$.

Preferred Values

$k_\infty = 6.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$, independent of temperature over the range 290–450 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 300–400 K.

Comments on Preferred Values

The preferred values are based on the results of the study of van den Bergh and Troe.[1]

References

[1] H. van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).

[2] H. van den Bergh, N. Benoit-Guyot, and J. Troe, Int. J. Chem. Kinet. **9**, 223 (1977).

[3] A. Mellouki, G. Laverdet, J. L. Jourdain, and G. Poulet, Int. J. Chem. Kinet. **21**, 1161 (1989).

[4] S. N. Buben, I. K. Larin, N. A. Messineva, and E. M. Trofimova, Kinet. Catal. **31**, 854 (1990); original pages 973–977 (1990).

$I + NO_3 \rightarrow IO + NO_2$
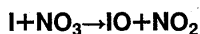
$\Delta H^\circ = -31 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.5 \pm 1.9) \times 10^{-10}$	298	Chambers, Heard, and Wayne, 1992[1]	DF-RF (a)

Comments

(a) Discharge flow system with resonance fluorescence detection of I atoms in the presence of excess NO_3 radicals. NO_3 radicals and I atoms were produced by the $F + HNO_3$ and $O + I_2$ reactions, respectively. NO_3 radical concentrations were measured by visible absorption spectroscopy. Corrections of up to 33% were applied to compensate for diffusion effects.

Preferred Values

No recommendation.

Comments on Preferred Values

The only reported measurement of this rate constant was made using the discharge flow technique at room temperature.[1] Difficulties were encountered due to wall reactions, and the pseudofirst-order plots exhibited pronounced curvature at contact times longer than 3 ms. Lancar *et al.*[2] state that they failed to observe a reaction between I atoms and NO_3 radicals. In view of these uncertainties, no recommendation is made for the rate coefficient at this time.

References

[1] R. M. Chambers, A. C. Heard, and R. P. Wayne, J. Phys. Chem. **96**, 3321 (1992).

[2] I. T. Lancar, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **177**, 554 (1991).

$I_2 + NO_3 \rightarrow I + IONO_2$
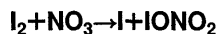
Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.5) \times 10^{-12}$	292–423	Chambers, Heard, and Wayne, 1992[1]	(a)

Comments

(a) Discharge flow system with simultaneous fluorescence detection of I_2 and visible absorption spectroscopic measurement of NO_3 radicals. NO_3 radicals were produced by the $F + HNO_3$ reaction. Pseudofirst-order conditions were used with NO_3 radical concentrations in excess over I_2. Experiments were performed to substantiate that I_2 loss was due to reaction with NO_3 radicals, and small corrections were made to compensate for diffusion effects; the overall error takes into account the uncertainties in the NO_3 radical concentrations ($+26\%$).

Preferred Values

$k = 1.5 \times 10^{-12} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$, independent of temperature over the range 290–430 K.

Reliability

$\Delta \log k = \pm 0.3$ over the temperature range 290–430 K.

Comments on Preferred Values

The only reported measurement of this rate constant[1] was made using the discharge flow technique and is the basis of the recommended value. Thermochemical data give a substantial endothermicity for $XONO_2$ formation in the reactions of the other halogens with the NO_3 radical, and the rapid rate of the $I_2 + NO_3$ reaction implies an upper limit of $\sim 29 \, \text{kJ mol}^{-1}$ for $\Delta H^\circ(IONO_2)$. Other possible channels giving $I + IO + NO_2$, $I + O_2 + INO$ or $IO + INO_2$ are all apparently endothermic.

References

[1] R. M. Chambers, A. C. Heard, and R. P. Wayne, J. Phys. Chem. **96**, 3321 (1992).

HO+HI→H₂O+I
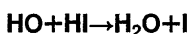
$\Delta H^\circ = -200.9 \, \text{kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.3 \pm 0.5) \times 10^{-11}$	295	Takacs and Glass, 1973[1]	DF-EPR
$(2.7 \pm 0.2) \times 10^{-11}$	298	Mac Leod *et al.*, 1990[2]	PLP-RF
$(3.3 \pm 0.2) \times 10^{-11}$	298	Lancar, Mellouki, and Poulet, 1991[3]	DF-EPR
$(7.0^{+1.9}_{-0.4}) \times 10^{-11} (T/298)^{-(1.5 \pm 0.5)}$	246–353	Campuzano-Jost and Crowley, 1999[4]	PLP-RF
$(6.5^{+2}_{-0.4}) \times 10^{-11}$	294		

Preferred Values

$k = 1.6 \times 10^{-11} \exp(440/T) \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ over the temperature range 240–360 K.

$k = 7.0 \times 10^{-11} \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

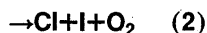$\Delta(E/R) = \pm 400 \, \text{K}$.

Comments on Preferred Values

The preferred values are based on the most recent and extensive study of Campuzano-Jost and Crowley,[4] in which, although the HI concentrations in the reaction cell were not monitored directly during the experiments, care was taken to remove potential impurities in the HI and a number of HO radical precursors were investigated before choosing H_2O_2 photolysis at 248 nm as the optimum. Additionally, two analyses using ion chromatography showed that the HI concentrations in the reaction cell were within ~ 20–25% of those expected.[4] The lower room temperature rate coefficients obtained in the studies of Mac Leod *et al.*[2] and Lancar *et al.*,[3] which are more than a factor of two higher than the earlier results of Takacs and Glass,[1] may have suffered from unrecognized losses of HI due to reactions with the HO radical precursors used and/or (in the study of Lancar *et al.*[3]) from generation of vibrationally excited HO radicals.[4]

References

[1] G. A. Takacs and G. P. Glass, J. Phys. Chem. **77**, 1948 (1973).

[2] H. Mac Leod, C. Balestra, J. L. Jourdain, G. Laverdet, and G. Le Bras, Int. J. Chem. Kinet. **22**, 1167 (1990).

[3] I. T. Lancar, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **177**, 554 (1991).

[4] P. Campuzano-Jost and J. N. Crowley, J. Phys. Chem. A **103**, 2712 (1999).
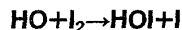
$HO+I_2 \rightarrow HOI+I$

$\Delta H° = -65 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.6^{+1.6}_{-0.8}) \times 10^{-10}$	298	Loewenstein and Anderson, 1985[1]	DF-RF
$(2.10 \pm 0.60) \times 10^{-10}$	240–348	Gilles, Burkholder, and Ravishankara, 1999[2]	PLP-LIF (a)
Relative Rate Coefficients			
$(2.3 \pm 0.3) \times 10^{-10}$	294	Jenkin, Clemitshaw, and Cox, 1984[3]	RR (b)

Comments

(a) From measurements of the rate coefficients at 240 K, 293–295 K, and 348 K, a least-squares analysis led to $k = 1.97 \times 10^{-10} \exp[(21 \pm 318)/T]$ cm^3 molecule^{-1} s^{-1}. The temperature independent expression cited in the table is preferred.[2]

(b) Steady-state photolysis of HONO–I$_2$–ethene–air (or N$_2$) mixtures at 1 bar total pressure. A rate coefficient ratio $k(HO+I_2)/k(HO+ethene) = 26.5 \pm 3.5$ was obtained from the rate of disappearance of ethene as a function of the I$_2$ concentration. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(HO+ethene) = 8.69 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 294 K and 1 bar of air.[4]

Preferred Values

$k = 2.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 240–350 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The reported room temperature rate coefficients of Loewenstein and Anderson,[1] Jenkin et al.,[3] and Gilles et al.[2] agree well, noting the large quoted error limits associated with the Loewenstein and Anderson[1] data. The preferred values are based on the most recent and extensive study of Gilles et al.[2]

References

[1] L. M. Loewenstein and J. G. Anderson, J. Phys. Chem. **89**, 5371 (1985).
[2] M. K. Gilles, J. B. Burkholder, and A. R. Ravishankara, Int. J. Chem. Kinet. **31**, 417 (1999).
[3] M. E. Jenkin, K. C. Clemitshaw, and R. A. Cox, J. Chem. Soc. Faraday Trans. 2 **80**, 1633 (1984).
[4] R. Atkinson, J. Phys. Chem. Ref. Data **26**, 215 (1997).

$NO_3+HI \rightarrow HNO_3+I$
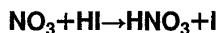
$\Delta H° = -128.5 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.3 \times 10^{-12} \exp[-(1830 \pm 300)/T]$	298–373	Lancar, Mellouki, and Poulet, 1991[1]	DF-EPR/MS (a)
$(2.5 \pm 0.8) \times 10^{-15}$	298		

Comments

(a) NO$_3$ radicals were generated by the reaction of F atoms with HNO$_3$. The rate coefficient was determined by measuring the decay rate of NO$_3$ radicals (by MS, cor-

recting for the contribution of HNO$_3$ to the $m/z = 62$ ion signal) or by measuring the formation rate of I atoms (by EPR).

Preferred Values

No recommendation.

Comments on Preferred Values

Although the rate coefficients measured in the only study[1] of this reaction from the decay of NO_3 using MS and I atom production using EPR spectrometry were in agreement,[1] there is a serious potential for secondary chemistry occurring in the system leading to an overestimation of the rate coefficient for the elementary process. Lancar *et al.*[1] reported that the reaction of $I+NO_3 \rightarrow IO+NO_2$ does not occur, while Chambers *et al.*[2] observed that the $I+NO_3$ reaction is rapid, with a measured rate coefficient of $k(I+NO_3)=4.5 \times 10^{-10} cm^3 molecule^{-1} s^{-1}$ at 298 K, and that I atoms are regenerated from subsequent reactions of IO radicals. Until this uncertainty is resolved, no recommendation can be made.

References

[1] I. T. Lancar, A. Mellouki, and G. Poulet, Chem. Phys. Lett. **177**, 554 (1991).

[2] R. M. Chambers, A. C. Heard, and R. P. Wayne, J. Phys. Chem. **96**, 3321 (1992).

$IO+HO_2 \rightarrow HOI+O_2$
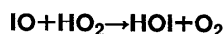
$\Delta H^\circ = -200 \, kJ \cdot mol^{-1}$

Rate coefficient data

$k/cm^3 molecule^{-1} s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.4\pm0.7)\times10^{-11}$	298	Jenkin, Cox, and Hayman, 1991[1]	MM (a)
$(1.03\pm0.13)\times10^{-10}$	298	Maguin *et al.*, 1992[2]	DF-MS (b)
$9.3\times10^{-12} exp[(680\pm110)/T]$	274–373	Cronkhite *et al.*, 1999[3]	(c)
$(9.7\pm2.9)\times10^{-11}$	298		

Comments

(a) Molecular modulation technique with UV absorption detection of HO_2 radicals at 220 nm and visible absorption detection of IO radicals at 427 nm. The radicals were produced by photolysis of O_3–CH_3OH–I_2–O_2 mixtures at 254 nm with HO_2 in excess over IO. The rate coefficient k was derived from a nonlinear least-squares analysis of absorption wave forms. The error limits do not include possible systematic errors.

(b) Discharge flow system with MS detection of HO_2 and IO radicals and HOI. IO and HO_2 radicals were produced by the $O(^3P)+I_2$ and $Cl+CH_3OH+O_2$ reactions, respectively. Pseudofirst-order decays of IO radicals were measured in the presence of excess HO_2. The cited value of k is the average of 25 experiments. HOI was shown to be a major product. The uniqueness of channel (1) could not be established, although no evidence was found for O_3 formation by the alternative channel of $IO+HO_2 \rightarrow HI+O_3$.

(c) Pulsed laser photolysis of Cl_2–CH_3OH–O_2–I_2–NO_2–SF_6–N_2 mixtures at 308 nm with simultaneous time-resolved detection of HO_2 radicals (by infrared TDLS) and IO radicals (by visible absorption spectroscopy). HO_2 radicals were generated by the reaction of Cl atoms (from photolysis of Cl_2) with CH_3OH in the presence of O_2, and IO radicals were generated by the reaction of $O(^3P)$ atoms (from photolysis of NO_2) with I_2.

Preferred Values

$k=8.8\times10^{-11} cm^3 molecule^{-1} s^{-1}$ at 298 K.

$k=9.0\times10^{-12} exp(680/T) cm^3 molecule^{-1} s^{-1}$ over the temperature range 270–380 K.

Reliability

$\Delta \log k=\pm0.2$ at 298 K.

$\Delta(E/R)=\pm300 \, K.$

Comments on Preferred Values

Although the studies of Maguin *et al.*[2] and Cronkhite *et al.*[3] provide more direct determinations of this rate coefficient than the earlier measurement of Jenkin *et al.*[3] using the molecular modulation technique, the error limits in the study of Cronkhite *et al.*[3] are substantial and their value of $k(298 K)$ is compatible both with the lower value of Jenkin *et al.*[1] and the higher value from Maguin *et al.*[2] Until more definitive studies are available, the preferred value at 298 K is taken as the mean of the rate coefficients obtained by Jenkin *et al.*,[1] Maguin *et al.*,[2] and Cronkhite *et al.*[3] The temperature dependence of Cronkhite *et al.*[3] is accepted, and the pre-exponential factor A is adjusted to fit the preferred 298 K rate coefficient.

The study of Maguin et al.[2] provides strong evidence that HOI is the major product. On the basis of current thermochemical data for the IO radical, the channel forming $HI + O_3$ is endothermic by $39\,kJ\,mol^{-1}$. The value of k at 298 K is consistent with the emerging reactivity pattern for the halogen oxide radicals with the HO_2 radical.

References

[1] M. E. Jenkin, R. A. Cox, and G. D. Hayman, Chem. Phys. Lett. **177**, 272 (1991).

[2] F. Maguin, G. Laverdet, G. Le Bras, and G. Poulet, J. Phys. Chem. **96**, 1775 (1992).

[3] J. M. Cronkhite, R. E. Stickel, J. M. Nicovich, and P. H. Wine, J. Phys. Chem. A **103**, 3228 (1999).

$$IO + ClO \rightarrow ICl + O_2 \quad (1)$$

$$\rightarrow Cl + I + O_2 \quad (2)$$

$$\rightarrow Cl + OIO \quad (3)$$

$$\rightarrow I + OClO \quad (4)$$

$$IO + ClO + M \rightarrow IOOCl + M \quad (5)$$

$\Delta H°(1) = -200\,kJ\cdot mol^{-1}$
$\Delta H°(2) = 10\,kJ\cdot mol^{-1}$
$\Delta H°(4) = -15\,kJ\cdot mol^{-1}$

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4 + k_5$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.1 \pm 0.2) \times 10^{-11}$	298	Bedjanian, Le Bras, and Poulet, 1997[1]	DF-MS (a)
$5.1 \times 10^{-12} \exp[(280 \pm 80)/T]$	200–362	Turnipseed et al., 1997[2]	(b)
$(1.29 \pm 0.27) \times 10^{-11}$	298		
Branching Ratios			
$k_1/k = 0.20 \pm 0.02$	298	Bedjanian, Le Bras, and Poulet, 1997[1]	(c)
$k_2/k = 0.25 \pm 0.02$	298		
$k_4/k = 0.55 \pm 0.03$	298		
$(k_1 + k_3)/k = 0.14 \pm 0.04$	298	Turnipseed et al., 1997[2]	(d)

Comments

(a) The rate coefficient k was determined from the decay of IO radicals in the presence of excess ClO under pseudofirst order conditions. The total pressure was 1.3 mbar He. k was measured in four different reaction mixtures using CF_3I and I_2 as sources of IO radicals, and $OClO$ and Cl_2O as sources of ClO radicals.

(b) Coupled DF-PLP system with LIF detection of IO radicals. IO radicals were photolytically generated in excess ClO, which was measured by UV absorption. The temporal profile of IO allowed accurate determination of k. I atoms were a major product, with a yield of 0.8 ± 0.2 at 298 K. Total pressure was 6.6–21 mbar of N_2–He. The quoted errors include estimates of systematic errors.

(c) Quantitative detection of reaction products $OClO$, Cl, and ICl, using both absolute and relative rate approaches to determine the branching ratios. The errors quoted are two least-squares standard deviations.

(d) Based on the ratio of the overall bimolecular rate coefficient determined from the first-order decay of IO in excess ClO (giving $k_1 + k_3$) with 4×10^{15} molecule cm^{-3} of O_3 present, to the total rate coefficient k determined in a similar manner with no excess O_3 present. At 223 K the yield of I atoms was 0.78 ± 0.25, suggesting that the I atom yield does not vary significantly with temperature over the range 223–298 K.

Preferred Values

$k = 1.2 \times 10^{-11}\,cm^3$ molecule^{-1} s^{-1} at 298 K.

$k = 4.7 \times 10^{-12} \exp(280/T)\,cm^3$ molecule^{-1} s^{-1} over the temperature range 200–370 K.

$k_1/k = 0.20$ at 298 K.
$k_2/k = 0.25$ at 298 K.
$k_4/k = 0.55$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

$\Delta(k_1/k) = 0.10$ at 298 K.

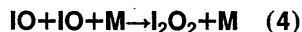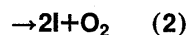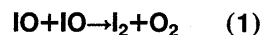$\Delta(k_2/k) = 0.10$ at 298 K.

$\Delta(k_4/k) = 0.10$ at 298 K.

Comments on Preferred Values

The two experimental studies of Bedjanian *et al.*[1] and Turnipseed *et al.*,[2] which used different techniques, give overall rate coefficients k which are in excellent agreement at 298 K. The recommended value is a simple mean of the two results.[1,2] The temperature dependence from Turnipseed *et al.*[2] is consistent with those observed for other exothermic XO+YO reactions and is accepted for the recommendation.

The quantitative information from the two studies[1,2] concerning the product channels is consistent within the cited uncertainties, with the discharge flow study of Bedjanian *et al.*[1] giving more detailed data and being used for the recommendation. The overall rate coefficient is accounted for by reactions (1)+(2)+(4) and it is concluded that reaction (3) is negligible. Provisionally, the branching ratios at 298 K can be applied to stratospheric temperatures since the I atom yield exhibits no significant temperature dependence.[2]

References

[1] Y. Bedjanian, G. Le Bras, and G. Poulet, J. Phys. Chem. A **101**, 4088 (1997).

[2] A. A. Turnipseed, M. K. Gilles, J. B. Burkholder, and A. R. Ravishankara, J. Phys. Chem. A **101**, 5517 (1997).

$$IO+BrO \rightarrow IBr+O_2 \quad (1)$$

$$\rightarrow Br+I+O_2 \quad (2)$$

$$\rightarrow Br+OIO \quad (3)$$

$$\rightarrow I+OBrO \quad (4)$$

$$IO+BrO+M \rightarrow IOOBr+M \quad (5)$$
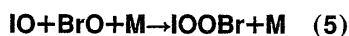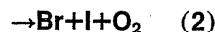
$\Delta H^\circ(1) = -195$ kJ·mol^{-1}

$\Delta H^\circ(2) = -17$ kJ·mol^{-1}

$\Delta H^\circ(4) = 23$ kJ·mol^{-1}

Rate coefficient data $(k=k_1+k_2+k_3+k_4+k_5)$

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.9\pm2.7)\times10^{-11}$	298	Laszlo *et al.*, 1997[1]	PLP-AS (a)
$k_1+k_3=2.5\times10^{-11}\exp[(260\pm100)/T]$	204–388	Gilles *et al.*, 1997[2]	PLP-LIF (b)
$k_1+k_3=6.0\times10^{-11}$	298		
$(8.5\pm1.5)\times10^{-11}$	298	Bedjanian, Le Bras, and Poulet, 1998[3]	DF-MS (c)
$k_1+k_3=(7.5\pm1.0)\times10^{-11}$	298		
$6.7\times10^{-12}\exp[(760\pm30)/T]$	210–333	Bloss, 1999[4]	(d)
$(8.49\pm1.40)\times10^{-11}$	295		
Branching Ratios			
$(k_2+k_4)/k<0.35$	298	Gilles *et al.*, 1997[2]	(b)
$k_1/k<0.05$	298	Bedjanian, Le Bras, and Poulet, 1998[3]	(e)
$k_2/k<0.3$	298		
$k_3/k=0.65-1.0$	298		
$k_4/k<0.2$	298		
$(k_2+k_4)/k<0.3$	298		
$k_1/k<0.2$	298	Bloss, 1999[4]	(f)
$k_4/k<0.15$	298		

Comments

(a) IO and BrO radicals were monitored at 427.2 and 338.5 nm, respectively, using resolutions of 0.3 and 0.6 nm and cross sections of 2.8×10^{-17} cm^2 molecule^{-1} and 1.4×10^{-17} cm^2 molecule^{-1}, respectively. The rate coefficient k was determined by a computer fit to complex kinetic decay curves. The total pressure was 260 mbar.

(b) IO radicals were detected by LIF. Pseudofirst order decays of IO radicals were measured in the presence of excess BrO and O$_3$. The reported rate coefficient applies only to the non-I-atom producing channels. An upper limit of 0.35 is suggested for the fraction of the overall reaction yielding I atoms at 298 K. Total pressure was 8 20 mbar.

(c) IO radical decays were monitored in the presence of excess BrO and O$_3$ to obtain the rate coefficient for the total non-I-atom forming channels. The total rate coefficient was obtained from simulations of the BrO, IO, and IBr profiles. The total pressure was 1 mbar.

(d) Pulsed laser photolysis with absorption spectroscopic detection of BrO and IO radicals using a time-resolved charge coupled detector (CCD) in the A–X systems at 300–350 nm and 400–470 nm, respectively. The IO radical cross section at 427.2 nm was measured to be $(1.9 \pm 0.17) \times 10^{-17}$ cm^2 molecule^{-1} (1.13 nm resolution) and the BrO radical differential cross sections were based on those measured by Wahner et al.[5] but increased in magnitude by 9% as recommended by Gilles et al.[2] and adjusted for a resolution of 1.13 nm. The rate coefficient k was determined by computer simulation of IO decays in excess BrO$_2$. The total pressure was 100–1000 mbar. Several experiments under varying conditions in the discharge flow system were used to establish the branching ratios.

(e) Several experiments under varying conditions in the discharge flow system were used to establish the branching ratios. The major channel produces Br+OIO with a branching ratio in the range given. Only upper limits were obtained for I atom and IBr formation.

(f) Based on the upper limits to the formation of the products IBr and OBrO, as measured by absorption spectroscopy. OIO was shown to be the major product.

Preferred Values

$k = 8.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 1.5 \times 10^{-11}$ exp(510/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200–390 K.

$k_3/k = 0.80$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 350$ K.

$\Delta(k_3/k) = 0.15$ at 298 K.

Comments on Preferred Values

The recent kinetic studies of this reaction by Laszlo et al.,[1] Gilles et al.,[2] Bedjanian et al.,[3] and Bloss[4] are in remarkably good agreement considering the experimental difficulties. Both Gilles et al.[2] and Bedjanian et al.[3] observed first-order kinetics for IO radical decays in excess BrO to obtain the rate coefficient for non-I-atom producing channels, $(k_1 + k_3) = (6.8 \pm 0.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The overall rate coefficients measured by Bedjanian et al.[3] and Bloss,[4] which were measured under complex kinetic conditions, are nevertheless in excellent agreement, giving $k = (8.5 \pm 1.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. These measurements give a value of $(k_1 + k_3)/k = 0.80 \pm 0.15$, which lies in the middle of the range suggested by Bedjanian et al.[3] for the branching ratio k_3/k. Considering that the IBr measurements of Bedjanian et al.[3] give $k_1/k < 0.05$, we recommend that $k_3/k = 0.80$ and that the total rate coefficient is that determined by Bedjanian et al.[3] and Bloss[4] at 298 K. The rate coefficient measurement of Laszlo et al.[1] is less precise but agrees within the experimental error limits with the recommendation.

The two studies of the temperature dependence[2,4] both show a negative activation energy for this radical+radical reaction. Although the temperature dependence of Gilles et al.[2] is derived from measurements of $k_1 + k_3$ over a wider temperature range, their result may not reflect the temperature dependence of the overall reaction if the branching ratio changes with temperature. The recommended temperature dependence is the simple mean of the two determinations of Gilles et al.[2] and Bloss,[4] with the pre-exponential factor A being adjusted to fit the preferred 298 K rate coefficient. The data do not allow a precise recommendation for the remaining branching between channels (1), (2), and (4). However, OBrO formation is not favorable on thermochemical grounds.

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$$IO+IO \rightarrow I_2+O_2 \quad (1)$$

$$\rightarrow 2I+O_2 \quad (2)$$

$$\rightarrow I+OIO \quad (3)$$

$$IO+IO+M \rightarrow I_2O_2+M \quad (4)$$

$\Delta H°(1) = -170 \text{ kJ} \cdot \text{mol}^{-1}$
$\Delta H°(2) = -18 \text{ kJ} \cdot \text{mol}^{-1}$

Rate coefficient data ($k = k_1 + k_2 + k_3 + k_4$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(8.0 \pm 1.8) \times 10^{-11}$	298	Laszlo, Kurylo, and Huie, 1995[1]	(a)
$(9.9 \pm 1.5) \times 10^{-11}$	250–320	Harwood et al., 1997[2]	(b)
$4.54 \times 10^{-11} \exp[(182 \pm 122)/T]$	250–320	Bloss, 1999[3]	(c)
$(8.2 \pm 1.0) \times 10^{-11}$	298		
$(9.3 \pm 1.0) \times 10^{-11}$	298	Vipond, 1999[4]	(d)
$(1.0 \pm 0.3) \times 10^{-10}$	295	Atkinson, Hudgens, and Orr-Ewing, 1999[5]	(e)
Branching Ratios			
$k_1/k < 0.05$	298	Sander, 1986[6]	(f)
$(k_2 + 0.5k_3)/k = 0.45$ at 28 mbar	298		
$(k_2 + 0.5k_3)/k = 0.18$ at 870 mbar	298		
$k_1/k < 0.05$	298	Laszlo, Kurylo, and Huie, 1995[1]	(a)
$(0.5k_3 + k_4) = 0.78$ at 1 bar	298	Harwood et al., 1997[2]	(g)
$k_1/k < 0.30$	298		
$k_1/k < 0.05$	298	Bloss, 1999[3]	(h)
$k_2/k = 0.11 \pm 0.04$	298		
$k_3/k = 0.38 \pm 0.08$	298		
$k_4/k = 0.46 \pm 0.06$	298		

Comments

(a) Pulsed laser photolysis with detection of IO radicals by absorption spectroscopy using the 4-0 band of the $A-X$ system at 427.2 nm, for which a cross section of $(2.8 \pm 0.5) \times 10^{-17}$ cm^2 molecule^{-1} was measured. The total pressure was 78–789 mbar of N$_2$. No prompt I$_2$ formation from IO decay was observed.

(b) Pulsed laser photolysis with detection of IO radicals by absorption spectroscopy using the 4-0 band of the $A-X$ system at 427.2 nm, for which a temperature-independent cross section of $(3.6 \pm 0.5) \times 10^{-17}$ cm^2 molecule^{-1} was measured. The total pressure was 78–789 mbar of N$_2$. No statistically significant temperature dependence of either k or σ was observed over the temperature range studied.

(c) Pulsed laser photolysis with detection of IO radicals by absorption spectroscopy using time-resolved CCD in the $A-X$ system at 400–470 nm. The cross section at 427.2 nm was measured to be $(1.9 \pm 0.17) \times 10^{-17}$ cm^2 molecule^{-1} (1.13 nm resolution), which decreased by ~45% on increasing the temperature from 220 to 335 K. The total pressure was 130–1000 mbar of N$_2$.

(d) Discharge flow system with LIF detection of I atoms after titration of IO radicals with NO. The total pressure was 2.5 mbar of He.

(e) Pulsed laser photolysis with detection of IO radicals by cavity ring-down spectroscopy using the 2-0 bandhead of the $A-X$ system at 445.02 nm, for which an absorption cross section of $(7.3 \pm 0.7) \times 10^{-17}$ cm^2 molecule^{-1} was measured. The total pressure was 12.4–40.2 mbar of Ar.

(f) Flash photolysis system with detection by absorption spectroscopy. The pressure dependence of the branching ratio to produce I atoms was based on the pressure dependence of k in the presence of excess O$_3$.

(g) Based on I$_2$ formation at short reaction times, and on comparison of rate coefficients measured in the presence and absence of O$_3$, with k (presence of O$_3$)/k(absence of O$_3$)=0.73 at 1 bar.

(h) Based on product absorptions due to I$_2$, OIO, and an unknown broadband absorption at $\lambda \leq 400$ nm assigned to I$_2$O$_2$. The value of σ(OIO) used was based on the branching ratio for the reaction IO+BrO$\rightarrow$Br+OIO determined by Bedjanian et al.[7]

Preferred Values

$k = 9.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 5.0 \times 10^{-11}$ exp(180/T) cm^3 molecule^{-1} s^{-1} over the temperature range 250–320 K.

$k_1/k \leqslant 0.05$ at 298 K.

$k_3/k = 0.38$ at 298 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

$\Delta(k_3/k) = \pm 0.08$ at 298 K.

Comments on Preferred Values

The recent studies[1–5] show good agreement for the overall rate coefficient at room temperature, which is higher than previously reported by Sander[6] and Barnes *et al.*[8] using discharge flow techniques and by Jenkin and Cox.[9] When the different values of the absorption cross sections are taken into account, there is much better agreement in the weighted values of k/σ. The preferred values are the mean of the results of Laszlo *et al.*,[1] Harwood *et al.*,[2] Bloss,[3] Vipond,[4] and Atkinson *et al.*[5]

All studies agree that the rate coefficient in the absence of excess O$_3$ is independent of pressure over the range 1–1000 mbar. However, Jenkin and Cox[9] and Sander[6] observed a falloff in k with decreasing pressure in the presence of excess O$_3$, i.e., when the I atom products are recycled to form IO. Bloss[3] observed OIO formation with a branching ratio of k_3/k in the range 0.30–0.48, based on an OIO absorption cross section of σ(OIO) $= 1.07 \times 10^{-17}$ cm^2 molecule^{-1} at 524 nm deduced from the OIO yield in the BrO+IO reaction.[7] The fraction of the IO+IO reaction leading to I atom production from these studies[3,6] appears to be ~20–30%, with

($k_2 + 0.5k_3$) ~0.2–0.3 consistent with the quantum yield for I$_2$ photosensitized decomposition of O$_3$.[10] All studies show that I$_2$ formation is minor, with $k_1/k < 0.05$.[1–3,6] Most authors have assumed that I$_2$O$_2$ is the other major product formed, although evidence for I$_2$O$_2$ formation is not unequivocal. Both Sander[6] and Bloss[3] report products that absorb in the UV near 300 nm but no direct identification of the absorbing species has been reported.

Temperature-dependent rate coefficients have been reported by Sander,[6] Harwood *et al.*,[2] and Bloss[3] The high value of $E/R = -(1020 \pm 200)$ K reported by Sander[6] reflects the large temperature coefficient obtained for σ. When the much weaker changes in σ are used (see data sheet on IO photolysis), the temperature dependence of k disappears. On balance the results of Bloss,[3] which take into account changes in the yield of IO radicals from the O+CF$_3$I reaction used to calibrate the absorptions, are preferred. The temperature dependence of Bloss[3] is used and the preexponential factor A is adjusted to fit the preferred 298 K rate coefficient.

References

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IO+NO→I+NO$_2$

$\Delta H^\circ = -66$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.67 \pm 0.16) \times 10^{-11}$	298	Ray and Watson, 1981[1]	DF-MS (a)
$(2.8 \pm 0.2) \times 10^{-11}$	298	Inoue *et al.*, 1983[2]	PLP-LIF
6.9×10^{-12} exp[(328±71)/T]	242–359	Daykin and Wine, 1990[3]	PLP-AS (b)
$(2.17 \pm 0.22) \times 10^{-11}$	298		
1.02×10^{-11} exp[(185±70)/T]	237–346	Turnipseed *et al.*, 1995[4]	PLP-LIF (c)
$(1.92 \pm 0.07) \times 10^{-11}$	298		
$(2.15 \pm 0.30) \times 10^{-11}$	298	Buben *et al.*, 1996[5]	DF-RF
$(1.9 \pm 0.5) \times 10^{-11}$	295	Atkinson, Hudgens, and Orr-Ewing, 1999[6]	PLP-AS (d)

Comments

(a) IO radicals were produced by the reaction $I+O_3$ and monitored by MS in an excess of NO.

(b) Pulsed laser photolysis of NO_2-I_2 mixtures at 351 nm. IO radical concentrations were monitored by long path absorption spectroscopy in an excess of NO. k was found to be independent of pressure over the range 50–260 mbar of N_2.

(c) Pulsed laser photolysis of N_2O-I_2 mixtures at 193 nm. IO radical concentrations were monitored by LIF in an excess of NO. k was found to be independent of pressure over the range 6.5–130 mbar of N_2.

(d) Pulsed laser photolysis of $N_2O-CF_3I-NO-Ar$ mixtures at 193 nm. IO radicals were monitored by cavity ring-down spectroscopy at 445.04 nm. k was found to be independent of pressure over the range 12.5–40 mbar of Ar.

Preferred Values

$k = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 9.0 \times 10^{-12}$ exp$(260/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 240–370 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

All of the available rate coefficient data for this reaction[1-6] are in reasonable agreement. The preferred value of k at 298 K is the mean of the values reported by Ray and Watson,[1] Inoue et al.,[2] Daykin and Wine,[3] Turnipseed et al.,[4] Buben et al.,[5] and Atkinson et al.[6] The preferred expression for k is obtained by taking the mean of the values of E/R of Daykin and Wine[3] and Turnipseed et al.[4] and combining it with a pre-exponential factor adjusted to give the preferred value of k at 298 K.

References

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$IO+NO_2+M \rightarrow IONO_2+M$

Low-pressure rate coefficients

Rate coefficient data

k_0 /cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.3 \pm 2.0) \times 10^{-31}$ [N$_2$]	277	Jenkin and Cox, 1985[1]	MM-A (a)
$7.7 \times 10^{-31}(T/300)^{-5.0}$ [N$_2$]	254–354	Daykin and Wine, 1990[2]	PLP-A (b)
$(3.6 \pm 1.0) \times 10^{-31}$ [N$_2$]	298	Maguin et al., 1992[3]	DF-MS (c)
$(7.9 \pm 2.2) \times 10^{-31}$ [N$_2$]	298		
$(1.80 \pm 0.07) \times 10^{-31}(T/300)^{-(2.6 \pm 0.5)}$ [O$_2$]	290–350	Larin et al., 1998[4]	(d)

Comments

(a) Photolysis of I_2 in the presence of O_3 was used to produce IO radicals, which were monitored by absorption at 427 nm in the presence of an excess of NO_2. The total pressure was varied over the range 47–537 mbar of N_2. The falloff curve was analyzed using $F_c = 0.4$ by analogy to the $BrO+NO_2+M$ reaction. A small correction was made for a second-order component to the IO radical kinetics at higher pressures.

(b) IO radicals were generated by the pulsed laser photolysis of $I_2-NO_2-N_2$ mixtures at 351 nm, and IO radicals were monitored by absorption at 427 nm. The association reaction was in the falloff regime over the pressure

(53–1000 mbar of N_2) and temperature ranges investigated. The data were extrapolated to the low- and high-pressure rate coefficients using $F_c = 0.4$.

(c) IO radicals and $IONO_2$ were detected by MS. IO radicals were generated by the reaction $O+I_2 \rightarrow IO+I$. The pressure range was 1.6–2.8 mbar of He. Using a relative third-body efficiency of N_2 and He for the analogous $BrO+NO_2+M$ reaction (ratio $k_0(N_2)/k_0(He)$ = 2.2) from Sander et al.,[5] the value reported above was derived.

(d) I atoms were generated by photolysis of a flow of CH_3I at 254 nm, and IO radicals were formed by the reaction $I+O_3 \rightarrow IO+O_2$. The pressure range was 1.3–8 mbar of

O_2. Assuming a ratio of $\beta_c(N_2)/\beta_c(O_2) = 1.4$, the expression $k_0 = 2.50 \times 10^{-31} \times (T/300)^{-2.6} [N_2] \, cm^3$ $molecule^{-1} s^{-1}$ over the temperature range 290–350 K was derived.

Preferred Values

$k_0 = 7.7 \times 10^{-31} (T/300)^{-5} [N_2] \, cm^3 \, molecule^{-1} s^{-1}$ over the temperature range 250–360 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

The preferred values for k_0 are based on the data of Daykin and Wine[2] and the value of Maguin et al.[3] derived with the given ratio of efficiencies for N_2 and He. The measurements of Larin et al.[4] are a factor of 4 lower than the preferred values and need to be confirmed.

High-pressure rate coefficients

Rate coefficient data

$k_\infty / cm^3 \, molecule^{-1} s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.6 \pm 0.6) \times 10^{-11}$	277	Jenkin and Cox, 1985[1]	MM-A (a)
1.55×10^{-11}	254–354	Daykin and Wine, 1990[2]	PLP-A (b)

Comments

(a) See comment (a) for k_0. The rate coefficient k_∞ was obtained from a fit of the falloff curve using $F_c = 0.4$.

(b) See comment (b) for k_0.

Preferred Values

$k_\infty = 1.6 \times 10^{-11} \, cm^3 \, molecule^{-1} s^{-1}$, independent of temperature over the range 250–360 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 250–360 K.

Comments on Preferred Values

The preferred values for k_∞ are based on the data of Jenkin and Cox[1] and Daykin and Wine.[2] Falloff extrapolations are made with $F_c = 0.4$, independent of temperature over the range 250–360 K.

References

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$INO + INO \rightarrow I_2 + 2NO$

$\Delta H° = 0.3 \, kJ \cdot mol^{-1}$

Rate coefficient data

$k / cm^3 \, molecule^{-1} s^{-1}$	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$8.4 \times 10^{-11} \exp(-2620/T)$	320–450	van den Bergh and Troe, 1976[1]	PLP-UVA
1.3×10^{-14}	298*		
$2.9 \times 10^{-12} \exp(-1320/T)$	298–328	Basco and Hunt, 1978[2]	FP-UVA
3.4×10^{-14}	298		

Preferred Values

$k = 1.3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.4 \times 10^{-11}$ exp$(-2620/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 300–450 K.

Reliability

$\Delta \log k = \pm 0.4$ at 298 K.

$\Delta(E/R) = \pm 600$ K.

Comments on Preferred Values

The results from the study of van den Bergh and Troe[1] are preferred over those from Basco and Hunt[2] because of a much wider range of conditions studied.

References

[1] H. van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).

[2] N. Basco and J. E. Hunt, Int. J. Chem. Kinet. **10**, 733 (1978).

INO$_2$+INO$_2$→I$_2$+2NO$_2$
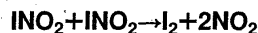
$\Delta H° = 8.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
1.7×10^{-14}	350	van den Bergh and Troe, 1976[1]	PLP-UVA

Preferred Values

$k = 4.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 2.9 \times 10^{-11}$ exp$(-2600/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 290–350 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

$\Delta(E/R) = \pm 1000$ K.

Comments on Preferred Values

The preferred values are based on the measured rate constant at 350 K from van den Bergh and Troe[1] and an assumed value for E/R equal to that for the reaction INO+INO→I$_2$+2NO (this evaluation). In the analogous reactions for other halogens this behavior appears to apply (see Ref. 1).

References

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HOI+ $h\nu$ →products
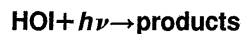
Primary photochemical processes

Reactions		$\Delta H°$/kJ·mol^{-1}	$\lambda_{threshold}$/nm
HOI+ $h\nu$ →HO+I	(1)	216	554
→HI+O(^{3}P)	(2)	345	347
→IO+H	(3)	404	296
→HI+O(^{1}D)	(4)	535	224

Absorption Cross-Section Data

Wavelength range/nm	Reference	Comments
280–500	Bauer *et al.*, 1998[1]	(a)
278–494	Rowley *et al.*, 1999[2]	(b)

Comments

(a) Laser photolysis of H_2O_2 at 248 nm was used to produce HO radicals in the presence of I_2, and hence to produce HOI *in situ*. Absorptions were measured by a gated diode array, and at selected wavelengths by a photomultiplier. The HOI concentration was determined from the instantaneous I_2 loss. The spectrum consists of two unstructured bands at 340.4 nm [σ_{max} $=(3.85 \pm 0.4) \times 10^{-19}$ cm^2 molecule^{-1}] and 406.4 nm [$\sigma_{max} = (3.30 \pm 0.3) \times 10^{-19}$ cm^2 molecule^{-1}].

(b) Same technique as in comment (a). Some irreproducibility in the 406 nm band was tentatively attributed to I_2O formation. Cross sections of $\sigma_{max} = 3.99 \times 10^{-19}$ cm^2 molecule^{-1} at 338.4 nm and $\sigma_{max} = 2.85 \times 10^{-19}$ cm^2 molecule^{-1} at 404.8 nm were obtained.

Quantum Yield Data

Quantum yield	Wavelength/nm	Reference	Comments
$\phi(1) = 1.05 \pm 0.13$	355	Bauer et al., 1998[1]	(a)

(a) HOI was produced by pulsed laser photolysis of HNO_3 at 248 nm to produce HO radicals in the presence of I_2. A second 355 nm laser pulse interrogated the HOI produced and the photofragment product HO was observed by resonance fluoroescence. Fresh reactants were introduced at each laser pulse. The quantity $\{\sigma^{HOI}\phi(HO)^{HOI}\}$ at 355 nm was determined, which with the measured value of σ (see above) gave the cited value of ϕ.

Preferred Values

Absorption cross sections of HOI at 295 K

λ/nm	$10^{19}\sigma/\text{cm}^2$	λ/nm	$10^{19}\sigma/\text{cm}^2$
280	0.0077	390	2.66
285	0.0226	395	2.98
290	0.0589	400	3.22
295	0.137	405	3.32
300	0.286	410	3.27
305	0.541	415	3.07
310	0.926	420	2.75
315	1.45	425	2.35
320	2.07	430	1.92
325	2.72	435	1.50
330	3.29	440	1.13
335	3.70	445	0.813
340	3.85	450	0.563
345	3.77	455	0.376
350	3.47	460	0.242
355	3.04	465	0.150
360	2.58	470	0.0904
365	2.21	475	0.0525
370	1.98	480	0.0296
375	1.94	485	0.0161
380	2.07	490	0.0086
385	2.33		

Quantum Yields

$\phi(1) = 1.0$ throughout the wavelength range 280–490 nm.

Comments on Preferred Values

The recommended values for the cross sections are those given by Bauer et al.[1] The data of Rowley et al.[2] are in good agreement with the exception of some systematically lower values in the 405 nm band.

References

[1] D. Bauer, T. Ingham, S. A. Carl, G. K. Moortgat, and J. N. Crowley, J. Phys. Chem. A **102**, 2857 (1998).

[2] D. M. Rowley, J. C. Mössinger, R. A. Cox, and R. L. Jones, J. Atmos. Chem. **34**, 137 (1999).

IO+hν→products

Primary photochemical processes

Reactions	$\Delta H°/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{threshold}$/nm
IO+$h\nu$→I+O(^{3}P) (1)	240	500
→I+O(^{1}D) (2)	430	280

Absorption cross-section data

Wavelength range/nm	Reference	Comment
427.2	Sander, 1986[1]	(a)
340–450	Laszlo, Kurylo, and Huie, 1995[2]	(b)
340–480	Harwood et al., 1997[3]	(c)
345–465	Bloss, 1999[4]	(d)

Comments

(a) Flash photolysis–absorption spectroscopy study. Cross sections at the head of the 4-0 band at 427.2 nm were measured at six temperatures in the range 250–373 K. A strong temperature dependence was observed at temperatures $<$315 K, with σ increasing with decreasing temperature.

(b) Pulsed laser photolysis–absorption spectroscopy study. A cross section of $\sigma(427.2\,\mathrm{nm}) = (2.8\pm0.5) \times 10^{-17}\,\mathrm{cm}^2\,\mathrm{molecule}^{-1}$ at 298 K was obtained, at a resolution of 0.3 nm.

(c) Pulsed laser photolysis–absorption spectroscopy study. Cross sections of $\sigma(427.2\,\mathrm{nm}) = (3.0\pm0.4) \times 10^{-17}\,\mathrm{cm}^2\,\mathrm{molecule}^{-1}$ and $(3.6\pm0.5) \times 10^{-17}\,\mathrm{cm}^2\,\mathrm{molecule}^{-1}$ were reported for resolutions of 0.44 and 0.14 nm, respectively, at 298 K.

(d) Pulsed laser photolysis of N_2O–CF_3I mixtures. IO radicals were detected by time-resolved CCD measurements of the postlaser pulse mixtures in the range 340–470 nm. Cross sections of $\sigma(427.2\,\mathrm{nm}) = (1.9\pm0.2) \times 10^{-17}\,\mathrm{cm}^2\,\mathrm{molecule}^{-1}$ (resolution of 1.13 nm) and $\sigma(396.5\,\mathrm{nm}) = (5.7\pm0.5) \times 10^{-18}\,\mathrm{cm}^2\,\mathrm{molecule}^{-1}$ were reported. The temperature dependence of the cross section at 427.2 nm was based on an analysis of the differential cross section, taking into account the temperature and pressure dependence of the yield of IO radicals from the $O(^3P)+CF_3I$ reaction.

Quantum Yield Data

No experimental data are available.

Preferred Values

Absorption cross sections for IO at 298 K

λ/nm	$10^{18}\sigma/\mathrm{cm}^2$	λ/nm	$10^{18}\sigma/\mathrm{cm}^2$
345	0.641	410	6.22
350	0.825	415	4.28
355	1.12	420	7.47
360	1.53	425	3.45
365	1.86	430	5.05
370	2.47	435	5.72
375	2.95	440	1.33
380	3.65	445	4.08
385	3.83	450	0.839
390	4.67	455	1.95
395	5.41	460	0.746
400	5.29	465	0.326
405	5.86		

Quantum Yields

$\phi(1) = 1.0$ throughout the wavelength range.

Comments on Preferred Values

Absorption Cross Sections. The recent measurements of the cross sections at the band head of the 4-0 band at 427.2 nm by Laszlo *et al.*,[2] Harwood *et al.*,[3] and Bloss[4] are in good agreement when the effects of resolution are taken into account. These data[2–4] confirm the earlier data of Sander,[1] Stickel *et al.*,[5] and Cox and Coker,[6] who all report the same value of $\sigma(427.2\,\mathrm{nm}) = 3.1 \times 10^{-17}\,\mathrm{cm}^2\,\mathrm{molecule}^{-1}$ for the 4-0 band at a resolution of 0.27 nm or less.

The study of Laszlo *et al.*[2] showed that the vibronic band structure is superimposed on a broad continuous absorption which maximizes at $\sim$400 nm. All three recent studies[2–4] confirm the presence of the underlying continuum, which makes an important contribution to atmospheric photolysis. Bloss[4] showed that IO absorption measurements in the 340–450 nm region are influenced by the presence of an underlying absorption due to a product of the IO+IO reaction, and this was accounted for in the reported values for σ.[4] The preferred values for the IO cross sections averaged over 5 nm intervals in the 345–465 nm range are therefore adopted from the Bloss[4] study.

The temperature dependence of $\sigma(427.2\,\mathrm{nm})$ has been investigated by Sander,[1] Harwood *et al.*,[3] and Bloss.[4] The studies of Harwood *et al.*[3] and Bloss[4] did not reproduce the large increase in σ with decreasing temperature below 315 K observed by Sander,[1] although values of σ above 315 K are in good agreement.[1,3,4] Bloss[4] showed that the yield of IO from the $O(^3P)+CF_3I$ reaction is pressure and temperature dependent, and this was accounted for in deriving the expression for the temperature dependence of $\sigma(427.2\,\mathrm{nm})$, which is adopted here. Harwood *et al.*[3] assumed a constant yield of IO from the $O(^3P)+CF_3I$ reaction which resulted in a temperature-independent cross section σ at 427.2 nm. Cross sections in the continuum region are assumed to be temperature and resolution independent.

Quantum Yields. Turnipseed *et al.*[7] observed LIF from the (0,0), (2,0), (3,0), and (2,1) bands of the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ transition of IO. The spectra are predissociated and the dissociation lifetime is $<$10 ns.[8] The lifetime of the upper state of IO formed in the A–X transition is thus so short that quenching, fluorescence and processes other than dissociation by reaction (1) must be negligible, and therefore the predominant fate of IO following light absorption is dissociation to O+I. Hence $\phi(1) = 1.0$.

References

[1] S. P. Sander, J. Phys. Chem. **90**, 2194 (1986).

[2] B. Laszlo, M. J. Kurylo, and R. E. Huie, J. Phys. Chem. **99**, 11701 (1995).

[3] M. H. Harwood, J. B. Burkholder, M. Hunter, R. W. Fox, and A. R. Ravishankara, J. Phys. Chem. A **101**, 853 (1997).

[4] W. Bloss, Ph.D. thesis, University of Cambridge, Cambridge, UK, 1999.

[5] R. E. Stickel, A. J. Hynes, J. D. Bradshaw, W. L. Chameides, and D. D. Davis, J. Phys. Chem. **92**, 1862 (1988).

[6] R. A. Cox and G. B. Coker, J. Phys. Chem. **87**, 4478 (1983).

[7] A. A. Turnipseed, M. K. Gilles, J. B. Burkholder, and A. R. Ravishankara, Chem. Phys. Lett. **242**, 427 (1995).

[8] G. Inoue, M. Suzuki, and N. Washida, J. Chem. Phys. **79**, 4730 (1983).

INO+hν→products

Primary photochemical transitions

Reactions	$\Delta H^\circ \cdot$ kJ mol^{-1}	$\lambda_{threshold}$/nm
INO+hν→I+NO	76	1570

Preferred Values

Absorption cross sections of INO at 298 K

λ/nm	$10^{17}\ \sigma/cm^2$	λ/nm	$10^{17}\ \sigma/cm^2$
230	1.4	380	0.065
235	5.3	390	0.078
238	7.0	400	0.92
245	6.5	410	1.10
251	5.9	420	0.10
260	2.4	430	0.094
270	1.0	440	0.080
300	0.09	450	0.060
360	0.045	460	0.040
370	0.059		

Comments on Preferred Values

The absorption cross-section values are the averages from the data of Refs. 1–3. The deviations between the results of these studies are only small. No quantum yield data are available. The photolysis quantum yield is expected to be unity over the whole wavelength range in view of the continuous nature of the absorption.

References

[1] H. van den Bergh and J. Troe, J. Chem. Phys. **64**, 736 (1976).
[2] N. Basco and J. E. Hunt, Int. J. Chem. Kinet. **10**, 733 (1978).
[3] E. Forte, H. Hippler, and H. van den Bergh, Int. J. Chem. Kinet. **13**, 1227 (1981).

INO₂+hν→products

Primary photochemical processes

Reactions	ΔH°/ kJ·mol^{-1}	$\lambda_{threshold}$/nm
INO₂+hν→I+NO₂	80	1500

Absorption cross-section data

Wavelength range/nm	Reference	Comment
200–400	Broske *et al.*, 1998[1]	(a)

Comments

(a) INO₂ was prepared by the photolysis of NO₂–I₂ mixtures with visible light at room temperature. Spectra were recorded with a diode array. Three broad bands were visible in the wavelength range covered, with σ

$=4.2\times10^{-18}$ cm^2 molecule^{-1} at 240 nm, σ=9.6 $\times10^{-19}$ cm^2 molecule^{-1} at 282 nm and σ=3.6 $\times10^{-19}$ cm^2 molecule^{-1} at 342 nm. The values of the cross sections are upper limits based on assuming stoichiometric conversion of NO₂ into INO₂.

Quantum Yield Data

No experimental data are available.

Preferred Values

Absorption cross sections of INO_2 at 298 K

λ/nm	10^{18} σ/cm^2	λ/nm	10^{18} σ/cm^2
210	2.36	305	0.308
215	1.87	310	0.247
220	1.96	315	0.251
225	2.79	320	0.275
230	3.47	325	0.325
235	3.99	330	0.312
240	4.22	335	0.349
245	4.00	340	0.373
250	3.30	345	0.373
255	2.34	350	0.298
260	1.62	355	0.295
265	0.996	360	0.271
270	0.871	365	0.207
275	0.898	370	0.149
280	0.996	375	0.074
285	0.922	380	0.024
290	0.810	385	0.00
295	0.620	390	0.00
300	0.373		

Comments on Preferred Values

The absorption cross-section values are provisional because no details have been reported. Although no quantum yield data are available, the continuous nature of the absorption suggests efficient dissociation of the I–NO$_2$ bond.

References

[1] R. Broske, Ph.D. thesis, University of Wuppertal, Wuppertal, Germany, 1999.

IONO$_2$+ *h*ν→products

Primary photochemical processes

Reactions	ΔH°/ kJ· mol^{-1}	λ$_{threshold}$ /nm
IONO$_2$+ *h*ν→IO+NO$_2$　　　(1)		
→I+NO$_3$　　　(2)		
→IONO+O(^{3}P)　(3)		
→IONO+O(^{1}D)　(4)		

Absorption cross-section data

Wavelength range/nm	Reference	Comment
200–400	Rowley *et al.*, 1999[1]	(a)

Comments

(a) IONO$_2$ was produced by the pulsed photolysis of NO$_2$–CF$_3$I mixtures at 355 nm (laser) and by a filtered Xe flashlamp at wavelengths >300 nm at room temperature. Time-resolved spectra were recorded with a CCD detector. Residual spectra after scaled subtraction of the identified absorbers NO$_2$, CF$_3$I, FNO, and COF$_2$ showed several broad overlapping features in the wavelength region covered. The values of the cross sections are lower limits because of the assumed stoichiometric conversion of CF$_3$I to IONO$_2$.

Quantum yield data

No experimental data are available.

Preferred Values

Absorption cross sections of $IONO_2$ at 298 K

λ/nm	$10^{17} \, \sigma/cm^2$	λ/nm	$10^{17} \, \sigma/cm^2$
200	2.26	310	0.40
205	2.06	315	0.38
210	1.61	320	0.36
215	1.39	325	0.36
220	1.21	330	0.35
225	1.22	335	0.34
230	1.21	340	0.33
235	1.21	345	0.31
240	1.20	350	0.30
245	1.13	355	0.28
250	1.10	360	0.27
255	0.99	365	0.25
260	0.86	370	0.22
265	0.80	375	0.20
270	0.72	380	0.18
275	0.72	385	0.15
280	0.68	390	0.13
285	0.62	395	0.11
290	0.58	400	0.09
295	0.53	405	0.07
300	0.48	410	0.06
305	0.45		

Comments on Preferred Values

The absorption cross-section values are provisional because no details have been reported. Although no quantum yield data are available, the continuous nature of the absorption suggests efficient dissociation of the $IO-NO_2$ bond.

References

[1] D. M. Rowley, R. A. Cox, and J. A. Mössinger (unpublished).

5. Appendix—Enthalpy Data

Most of the thermochemical data have been taken from evaluations or reviews. In some cases, we have selected more recent experimental data, which appear to be reliable. The error limits are those given by the original author or reviewer.

Enthalpy Data

Species	$\Delta_f H^\circ_{298}$/ kJ·mol⁻¹	$\Delta_f H^\circ_0$/ kJ·mol⁻¹	Reference
H	217.998±0.006	216.03±0.006	1
H₂	0	0	1
O(³P)	249.18±0.10	246.79±0.10	1
O(¹D)	438.9	436.6	2
O₂	0	0	1
O₂(¹Δ)	94.3	94.3	2
O₂(¹Σ)	156.9	156.9	2
O₃	142.7	145.4	3
HO	39.3±2.1	39.0±2.1	4
HO₂	14.6		4
H₂O	−241.826±0.04	−238.92±0.04	1
H₂O₂	−136.31	−130.04	3
N	472.68±0.40		1
N₂	0	0	1
NH	352±10		5
NH₂	188.7±1.3		4
NH₃	−45.94±0.35		1
NO	90.25	89.75	3
NO₂	33.18	35.98	3
NO₃	73.72±1.4	78.95±1.4	6
N₂O	82.05	85.500	3
N₂O₄	9.1±1.7	18.7±1.7	7
N₂O₅	11.3		6,7
HNO	112.95±0.25	110.02±0.25	8
HNO₂	−79.5		3
HNO₃	−135.06	−125.27	3
HO₂NO₂	−57.24		9
CH	596.4±1.2		4
CH₂(³B₁)	390.4±4		4
CH₂(¹A₁)	428.3±4		4
CH₃	146.4±0.4		4
CH₄	−74.81	−66.818	3
CN	441.4±4.6		4
HCN	135±8		7
HCO	43.1		10,11
CH₂O	−108.6	−104.7	2
CH₃O	17.2±3.8		4
CH₂OH	−17.8±1.3	−11.5±1.3	12
CH₃OH	−201.6±0.2		13
CO	−110.53±0.17		1
NCO	127.0		4
HOCO	−217±10	−205±10	4,14
HCOOH	−378.8±0.5	−371.6	13
CH₃O₂	9.0±5.1		4
CH₃OOH	−131		7
HOCH₂O₂	−162.1±2.1		15
CH₃ONO	−65.3		16
CH₃ONO₂	−119.7		16
CH₃O₂NO₂	−44		9
CO₂	−393.51±0.13		1
C₂H	566.1±2.9		4
C₂H₂	228.0±1.0		13
C₂H₃	300.0±3.4		4

Enthalpy Data—Continued

Species	$\Delta_f H^\circ_{298}$/ kJ·mol⁻¹	$\Delta_f H^\circ_0$/ kJ·mol⁻¹	Reference
C₂H₄	52.2±1.2		13
C₂H₅	120.9±1.6		4
C₂H₆	−84.0±0.2		13
CH₂CN	243.1±11.3		4
CH₃CN	64.3±26.3		17
CH₂CO	−47.7±1.6		18
CH₃CO	−10.0±1.2		4
CH₂CHO	10.5±9.2		4
CH=CHOH		120±10	19
CH₃CHO	−165.8±0.4		13,17
C₂H₅O	−15.5±3.4		4
C₂H₄OH		−23±6	19
CH₃CHOH	−51.6		4
C₂H₅OH	−234.8±0.2		13,17
(CHO)₂	−211.9±0.8		13,17
CH₃CO₂	−207.5±4		4
CH₃CO₂H	−432.14±0.4		13,17
C₂H₅O₂	−27.4±9.9		4
CH₃OOCH₃	−125.7±1.3		13,17
CH₃C(O)O₂	−172±20		4
C₂H₅ONO	−103.8		13,17
C₂H₅ONO₂	−154.1±1.0		13,17
C₂H₅O₂NO₂	−63.2		20
CH₃C(O)O₂NO₂	−258±22		21
CH₂=CHCH₂	170.7±8.8		4
C₃H₆	20.2±0.4		13,17
n-C₃H₇	100.8±2.1		4
i-C₃H₇	86.6±2.0		4
C₃H₈	−104.5±0.3		13,17
C₂H₅CO	−32.3±4.2		22,23
CH₃COCH₂	−23.9±10.9		4
C₂H₅CHO	−187.4±1.5		13,17
CH₃COCH₃	−217.2±0.4		13,17
C₃H₆OH	−74		16
n-C₃H₇O	−41.4		4
i-C₃H₇O	−52.3		4
i-C₃H₇OH	−272.5±0.4		13,17
CH₃COCHO	−271.1±4.7		13,17
C₃H₅O₂	87.9±5.5		4
i-C₃H₇O₂	−68.8±11.3		4
n-C₃H₇ONO₂	−174.1±1.3		13,17
i-C₃H₇ONO₂	−190.8±1.7		13,17
n-C₄H₉	80.9±2.2		4
s-C₄H₉	66.7±2.1		4
n-C₄H₁₀	−125.7±0.4		13
n-C₃H₇CHO	−204.8±1.5		13
CH₃COC₂H₅	−238.5±0.5		13
n-C₄H₉O	−62.8		4
s-C₄H₉O	−69.5±3.3		4
S	277.17±0.15		1
HS	143.01±2.85	142.55±3.01	24
H₂S	−20.6±0.5		1
HSO	−4		4
SO	5.0±1.3	5.0±1.3	7
HSO₂	−222		4
SO₂	−296.81±0.20		1
HOSO	−385		4
SO₃	−395.72	−389.99	3
HSNO	94		25
CH₃S	124.60±1.84		24
CH₃SH	−22.9±0.6		26
CH₃SCH₂	136.8±5.9		4

Enthalpy Data—Continued   *Enthalpy Data—Continued*

Species	$\Delta_f H^\circ_{298}$/ kJ·mol⁻¹	$\Delta_f H^\circ_0$/ kJ·mol⁻¹	Reference
CH₃SCH₃	−37.24	−21.058	3
CS	278.5±3.8		4
CH₃SO	−67±10		27
CH₃SOO	75.7±4.2	87.9±4.6	28
OCS	−142.09	−142.218	3
S₂	128.60		1
CH₃SS	68.6±8		4
CH₃SSCH₃	−24.3		29
CS₂	117.36	116.57	3
HOCS₂	110.5±4.6		30
F	79.38±0.30		1
HF	−273.30±0.70		1
HOF	−98.3±4.2	−95.4±4.2	7
FO	109±10	108±10	7
FO₂	25.4±2	27.2±2	7
FONO	67		31
FNO₂	−108.8		9
FONO₂	10	18	7
CH₂F	−31.8±8.4		4
CH₃F	−232.6		32
CH₃CH₂F	−263±2		33
HCOF		−392.5±6.3	34
FCO	−152.1±12	−172±63	4
F₂	0	0	1
CHF₂	−238.9±4		4
CH₂F₂	−453±8		33
CH₃CHF₂	−501±6		33
CF₂	−184.1±8.4		4
COF₂	−634.7	−631.57	3
CHF₃	−697.6		33
CF₃	−466.1±3.8		4
CH₂CF₃	−517.1±5.0		4
CH₃CF₃	−748.7±3.2		35
CH₂FCHF₂	−691±10		35
CF₃O	−655.6±6.3		36
CF₃OH	−923.4±13.4		37
CF₃OF	−785		33
CF₃O₂	−614.0±15.4		15
CF₃CO₂H	−1031		26
CF₃O₂NO₂	−686		20
CF₄	−933	−927	38
Cl	121.301±0.008		1
HCl	−92.31±0.10		1
HOCl	−78	−75	2,39
ClO	101.63±0.1		7
ClOO	97.457	99.128	40
OClO	95.6±1.3		41,42
sym-ClO₃	232.6±17		43
ClNO	51.7	53.6	7
ClNO₂	12.5	17.95	3
ClONO	56		9
ClONO₂	22.9±2.2		44
CH₂Cl	117.3±3.1		4
CH₂ClO₂	−5.1±13.6		4
CH₃Cl	−81.96±0.67	−74.04±0.67	38
CHF₂Cl	−483.7±5.9		45
CH₃CHFCl	−313.4±2.6		35
CH₃CF₂Cl	−536.2±5.2		35
ClCO	−21.8±2.5	−23.4±2.9	46
COFCl	−427	−423	7
CFCl	31.0±13.4		4
CF₂Cl	−279.1±8.3		4

Species	$\Delta_f H^\circ_{298}$/ kJ·mol⁻¹	$\Delta_f H^\circ_0$/ kJ·mol⁻¹	Reference
CF₂ClO₂	−406.5±14.6		15
CF₂ClO₂NO₂	−480		47
CF₃Cl	−707.9±3.8	−702.8±3.8	45
Cl₂	0	0	1
Cl₂O	77.2±3.4		48
Cl₂O₂	127.6±2.9		42
Cl₂O₃	153		49
CCl₂	230.1±8.4		4
CHCl₂	89.0±3.0		4
CHCl₂O₂	−19.2±11.2		4
CH₂Cl₂	−95.4±0.8	−88.5±0.8	38
CHFCl₂	−284.9±8.8		45
COCl₂	−220.1	−218.4	7
CFCl₂	−89.1±10.0		4
CFCl₂O₂	−213.7		4
CFCl₂O₂NO₂	−287.4		47
CF₂Cl₂	−493.3±2.5	−489.1±2.5	45
CH₂ClCF₂Cl	−543±10		33
CF₃CHCl₂	−740±10		33
CF₂ClCHFCl	−724±10		33
CF₂ClCF₂Cl	−925.5±4.3		35
CCl₃	71.1±2.5	69.9±2.5	50
CCl₃O₂	−20.9±8.9		4
CCl₃O₂NO₂	−83.7		47
CHCl₃	−103.3±1.3		7
C₂HCl₃	−7.78	−4.318	3
CH₃CCl₃	−144.6±0.8		35
CFCl₃	−284.9±1.7	−281.1	45
CF₂ClCFCl₂	−726.8±2.8		35
CCl₄	−95.8±0.6	−93.6±0.6	38
C₂Cl₄	−12.4	−11.9	7
C₂Cl₅	33.5±5.4	33.9±6.3	51
Br	111.87±0.12		1
HBr	−36.29±0.16		1
HOBr	⩾−56		52
BrO	120±6		53
OBrO	152±25	161±25	7
BrOO	108±40	116±40	7
BrNO	82.17	91.46	3
BrONO₂	47		9
CH₂Br	169.0±4.2		4
CH₃Br	−38.1±1.3		54
CF₃Br	−650		33
CF₂ClBr	−438±8		33
BrCl	14.6±1.3	22.1±1.3	7
Br₂(g)	30.91		1
Br₂O	107.1±3.5		55
Br₂O₂	181±12		56
CHBr₂	188.2±9.2		4
CF₂Br₂	−379±8		33
CF₂BrCF₂Br	−789.9		35
CHBr₃	23.8±4.5		54
I	106.76±0.04		1
IH	26.50		1
HOI	−69.6±5.4	−64.9	57,58
IO	116±5		59
INO	121.3±4.2	124.3±4.2	60
INO₂	60.2±4.2	66.5±4.2	60
CH₂I	230.1±6.7		4
CH₃I	14.2±0.9		13
CF₃I	−589.1±3.3		7
ICl	17.5±0.1	19.1±0.1	7
IBr	40.9±0.1	49.8±0.1	7
I₂(g)	62.42±0.08		1

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